

AFWAL-TR-86-4090

ADA179775

THERMOSET HIGH-TEMPERATURE SYSTEMS BASED ON THE HOMOLYTIC  
POLYMERIZATION OF BENZOCYCLOBUTENE AROMATIC IMIDE MONOMERS  
AND OLIGOMERS



L. S. Tan  
University of Dayton Research Institute  
Dayton, OH 45469-0001

F. E. Arnold  
Polymer Branch  
Nonmetallic Materials Division

June 1986

Final Report for Period 1 September 1984 to 30 March 1986

Approved for public release; distribution unlimited.

MATERIALS LABORATORY  
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6533

20040219201

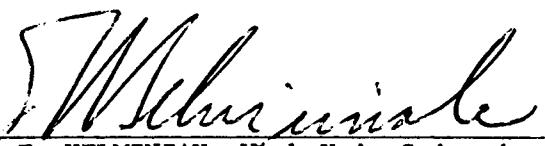
BEST AVAILABLE COPY

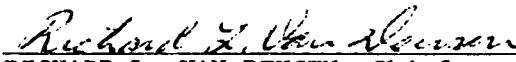
NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is released to the National Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
T. E. HELMINIAK, Work Unit Scientist  
Polymer Branch  
Nonmetallic Materials Division

  
RICHARD L. VAN DEUSEN, Chief  
Polymer Branch  
Nonmetallic Materials Division

FOR THE COMMANDER

  
MERRILL L. MINGES, Chief  
Nonmetallic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization, please notify AFWAL/MLBP, Wright-Patterson AFB, OH 45433-6533 to help us maintain a current mailing list."

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>		1b. RESTRICTIVE MARKINGS													
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.													
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE															
4. PERFORMING ORGANIZATION REPORT NUMBER(S) <b>AFWAL-TR-86-4090</b>		5. MONITORING ORGANIZATION REPORT NUMBER(S)													
6a. NAME OF PERFORMING ORGANIZATION <b>AFWAL Polymer Branch</b>	6b. OFFICE SYMBOL (If applicable) <b>AFWAL/MLBP</b>	7a. NAME OF MONITORING ORGANIZATION													
6c. ADDRESS (City, State and ZIP Code) <b>AFWAL/MLBP Wright-Patterson AFB, OH 45433</b>		7b. ADDRESS (City, State and ZIP Code)													
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER													
8c. ADDRESS (City, State and ZIP Code)		10. SOURCE OF FUNDING NOS. <table border="1"><tr><td>PROGRAM ELEMENT NO. <b>61102F</b></td><td>PROJECT NO. <b>2303</b></td><td>TASK NO. <b>Q3</b></td><td>WORK UNIT NO. <b>07</b></td></tr></table>		PROGRAM ELEMENT NO. <b>61102F</b>	PROJECT NO. <b>2303</b>	TASK NO. <b>Q3</b>	WORK UNIT NO. <b>07</b>								
PROGRAM ELEMENT NO. <b>61102F</b>	PROJECT NO. <b>2303</b>	TASK NO. <b>Q3</b>	WORK UNIT NO. <b>07</b>												
11. TITLE (Include Security Classification) <b>Thermoset High-Temperature Systems Based</b>															
12. PERSONAL AUTHOR(S) <b>Leon-Seng Tan and Fred E. Arnold</b>															
13a. TYPE OF REPORT <b>Final</b>	13b. TIME COVERED <b>FROM 9/1/84 TO 3/30/86</b>	14. DATE OF REPORT (Yr., Mo., Day) <b>1986 June</b>	15. PAGE COUNT <b>41</b>												
16. SUPPLEMENTARY NOTATION															
17. COSATI CODES <table border="1"><tr><th>FIELD</th><th>GROUP</th><th>SUB. GR.</th></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>	FIELD	GROUP	SUB. GR.										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) <b>Thermosets Benzocyclobutene High Temperature Imide</b>		
FIELD	GROUP	SUB. GR.													
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>A new series of bisbenzocyclobutene-terminated aromatic imide oligomers has been synthesized from the condensation reaction of 4-aminobenzocyclobutene and the perspective dianhydride in refluxing acetic acid/toluene. The differential scanning calorimetric studies of the foregoing monomers indicated that polymerization exotherms began at 229–250°C and reached their maxima at 258–263°C. The cured samples (250°–254°C; N<sub>2</sub>; 8 hrs) were surprisingly stable toward thermooxidative degradation; only 7- to 10-percent weight loss was observed after 200 hrs (in air) at 314°C (600°F).</p>															
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <b>UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/></b>		21. ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>													
22a. NAME OF RESPONSIBLE INDIVIDUAL <b>T. E. Helminiak</b>		22b. TELEPHONE NUMBER (Include Area Code) <b>(513) 255-9155</b>	22c. OFFICE SYMBOL <b>AFWAL/MLBP</b>												

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

Block 11 (Continued)

on the Homolytic Polymerization of Benzocyclobutene Aromatic Imide Monomers and Oligomers.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

## FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr T. E. Helminiak as the ML Project Scientist. Coauthors were Dr F. E. Arnold, Materials Laboratory (AFWAL/MLBP) and Dr Loon-Seng Tan, University of Dayton Research Institute.

This report covers research conducted from September 1984 to March 1986.

The authors wish to extend thanks to Edward Soloski, Marlene Houtz and Dr Ivan J. Goldfarb for their contributions to thermal analysis. We also thank Dr Chi K. Yu (mass-spectroscopic characterization), Dr E. Grant Jones (TGA/MS), and Charles Benner (HPLC). A gift of 2,2'-bis(3-aminophenyl) hexafluoropropane from Dr W. H. Mueller and Mr G. D. Pasek (American Hoechst Corporation) is gratefully acknowledged.

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	RESULTS AND DISCUSSION	3
	A. Synthesis	3
	B. Thermal Analysis	5
III	CONCLUSION	17
IV	EXPERIMENTAL	19
	Preparation of Bis-2, 2-(N-4-benzocyclobutenyl phthalimido)hexafluoropropane (7a)	19
	Preparation of 2,2-bis[4-(N-4'-benzocyclobutenyl-4"-phenoxyphthalimido)]hexafluoropropane (7b)	20
	Preparation of Bis-[4-(N-4'-benzocyclobutenyl-4"-phenoxyphthalimido)]sulfone (7c)	23
	Preparation of oligomeric mixture (10a)	27
	Preparation of oligomeric mixture (10b)	27
	Preparation of oligomeric mixture (10c)	33
	Preparation of oligomeric mixture (10d)	36
	REFERENCES	40

## LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	DSC thermogram of bis-2,2-(N-4-benzocyclobutenyl phthalimido) hexafluoropropane (7a)	8
2	Isothermal aging studies of the thermosetting resin derived from bis-2,2-(N-4-benzocyclobutenyl phthalimido) hexafluoropropane (7a) at 600°F (316°C), 650°F (343°C), and 700°F (371°C) under circulating air	11
3	The structural representations of the thermosetting polymers derived from the solid state homopolymerization of benzocyclobutene-based starting materials	14
4	$^1\text{H}$ NMR spectrum of bis-2,2-(N-4 benzocyclo-but enylphthalimido) hexafluoropropane (7a)	21
5	Infrared spectrum of bis-2,2-(N-4 benzocyclo-but enylphthalimido) hexafluoropropane (7a)	22
6	$^1\text{H}$ NMR spectrum of 2,2-bis[4-(N-4'-benzocyclo-but enyl-4"-phenoxyphthalimido)] hexafluoropropane (7b)	24
7	Infrared spectrum of 2,2-bis[4-(N-4'-benzocyclo-but enyl-4"-phenoxyphthalimido)] hexafluoropropane (7b)	25
8	$^1\text{H}$ NMR spectrum of bis [4-(N-4'-benzocyclobut enyl-4"-phenoxyphthalimido)] sulfone (7c)	26
9	Infrared spectrum of bis[4-(N-4'-benzocyclo-but enyl-4"-phenoxyphthalimido)] sulfone (7c)	28
10	$^1\text{H}$ NMR spectrum of oligomer (10a)	29
11	Infrared spectrum of oligomer (10a)	30
12	$^1\text{H}$ NMR spectrum of oligomer (10b)	31
13	Infrared spectrum of oligomer (10b)	32
14	$^1\text{H}$ NMR spectrum of oligomer (10c)	34
15	Infrared spectrum of oligomer (10c)	35
16	$^1\text{H}$ NMR spectrum of oligomer (10d)	38
17	Infrared spectrum of oligomer (10d)	39

**LIST OF TABLES**

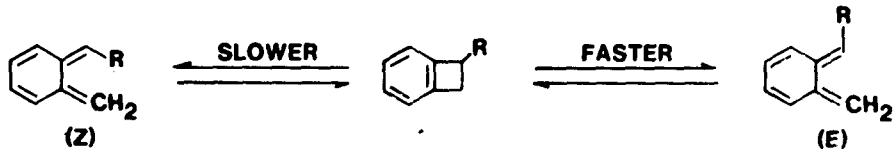
<b>TABLE</b>		<b>PAGE</b>
1	<b>Thermal Properties</b>	9
2	<b>Thermal Characteristics</b>	9

## SECTION I

### INTRODUCTION

A variety of high-temperature polymeric systems has been prepared in the last decade of new materials research. Promising systems include the aromatic and aromatic/heterocyclic class of materials. Although such polymer systems exhibit excellent thermal and thermo-oxidative stabilities, they are formed by polycondensation reactions and exhibit very high glass transition temperatures ( $T_g$ ) which present problems in processing. Some do not even exhibit a  $T_g$ , so polycondensations are not likely to present viable approaches. A reactive oligomer exhibiting the required  $T_g$  and flow characteristics may offer a viable approach to provide an ultrahigh temperature (650-700°F) matrix resin. The oligomeric structure could be tailored to satisfy the high-temperature thermoset system. Investigation to discover new addition reactions which can produce molecular structures with 650-700°F stability is required to impact this technology.

Cure chemistry utilizing a strained four-membered ring fused to an aromatic system would provide a thermally-induced addition reaction. Indeed, the utilization of a biphenylene moiety in the backbones of polyaromatic ether-ketones and ether-ketone-sulfones<sup>1</sup>, as well as in polyquinolines and polyquinoxalines<sup>2</sup>, as the crosslinking group has been reported. An example of a polyimide, using biphenylene as end-capping group has also appeared recently<sup>3</sup>. We have found that a close counterpart of biphenylene, namely benzocyclobutene<sup>4</sup>, can function very well as a polymerizable unit at a much lower temperature (about 250°C vs 380-400°C for biphenylene). It has been established that under appropriate thermal condition, the strained four-membered ring of benzocyclobutene undergoes electrocyclic ring opening<sup>5</sup>.



In the presence of a suitable dienophile, the more reactive form, i.e., o-xylylene (or o-quinodimethane) will be engaged in a Diels-Alder reaction<sup>5-10</sup>; otherwise, it will react with itself. On account of such versatile reactivities, benzocyclobutene has been an invaluable building block in the construction of [2n] cyclophane<sup>8</sup> and other complex organic molecules<sup>5</sup> as well as in natural product synthesis<sup>10</sup>. This report describes our work on the synthesis and characterization of series of bis(benzocyclobutene)-terminated aromatic imide monomers and oligomers<sup>11</sup>.

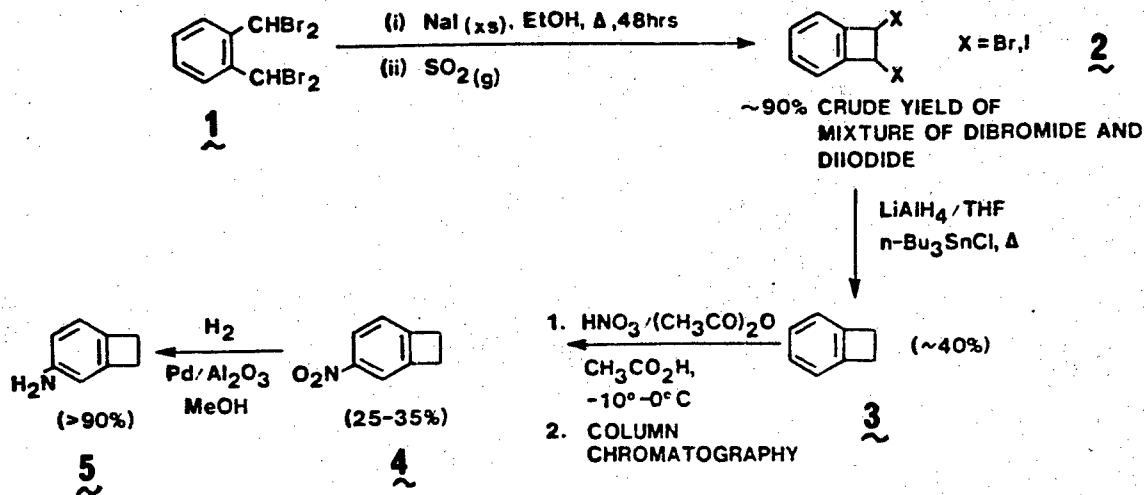
SECTION II  
RESULTS AND DISCUSSION

**A. Synthesis**

The end-capping agent, i.e., 4-aminobenzocyclobutene was prepared in a four-step synthetic sequence following procedures adapted from literature<sup>12-15</sup>. (See Scheme I.)

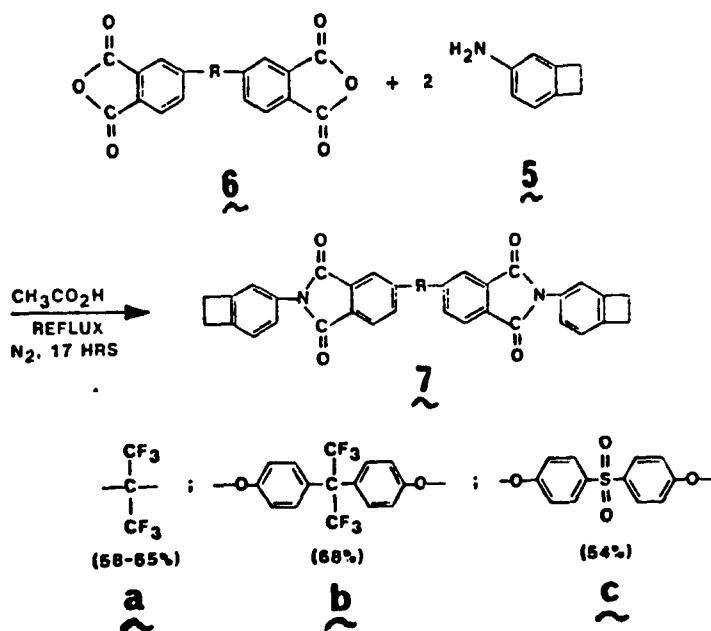
Although the hydrogen chloride salt of 4-aminobenzocyclobutene is stable under normal conditions, the parent amine, which is a faint amber liquid when freshly prepared, gradually turns dark over a period of 24 hrs. In the preparation of the bis-(benzocyclobutene) aromatic imide monomers and oligomers, 4-aminobenzocyclobutene, 5 was used immediately after isolation.

**Scheme I**



Refluxing a mixture of 5 and the prospective dianhydride 6 in acetic acid under N<sub>2</sub> for about 17 hrs led to the isolation of the desired bisbenzocyclobutene aromatic imide monomers, 7a-c, which were purified by column chromatography 54-68 percent). (See Scheme II.)

Scheme II



The yields of 7a-c can be improved moderately if (a) a Dean-Stark trap was used to remove the water of imidization azeotropically with toluene, and (b) the crude products were filtered through a bed of silica gel, instead of

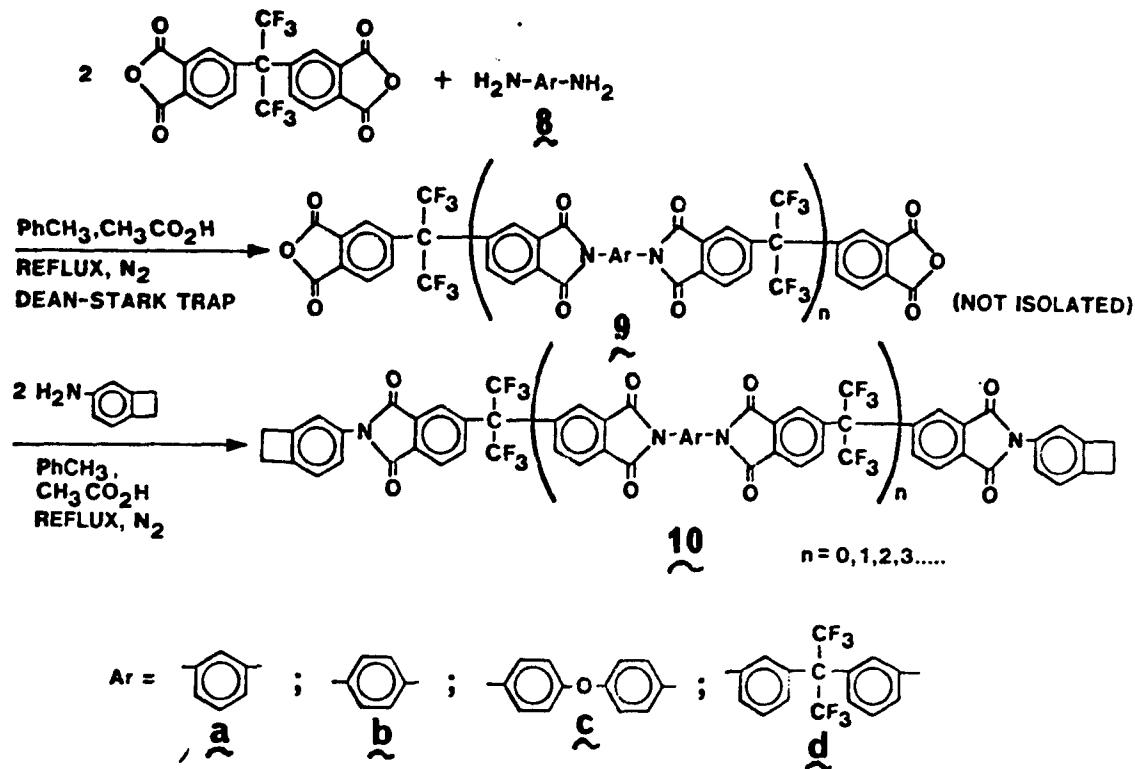
purified by column chromatography.

The bisbenzocyclobutene aromatic imide oligomers were prepared as follows. An 1:2 stoichiometric mixture of an aromatic diamine and bis-2,2-(4-phthalic anhydrido) hexafluoropropane was refluxed in boiling acetic acid/toluene under N<sub>2</sub> for about 17 hrs. Water of imidization was removed azeotropically from the reaction mixture. Freshly prepared 4-aminobenzocyclobutene, in slight excess, was subsequently added to the cooled reaction mixture. The ensuing reflux (17 hrs) of the reaction mixture completed the end-capping of the aromatic imide oligomers. Purification of the crude products by passing the CH<sub>2</sub>Cl<sub>2</sub> solution through a small column packed with hexane saturated silica and eluting with hexane or petroleum ether provided the imide oligomers as yellow to amber microcrystalline solids. (See Scheme III.)

#### B. Thermal Analysis

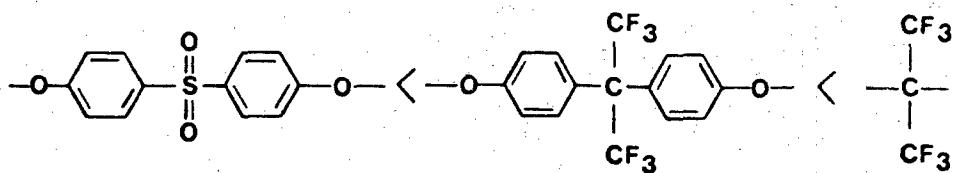
The thermal characteristics and stabilities of the bisbenzocyclobutene aromatic imide monomers and oligomers as well as the corresponding thermosetting resins were determined by the differential scanning calorimetry (DSC), and thermomechanical analysis (TMA). The long-term and short-term thermooxidative stabilities were assessed by the isothermal gravimetric analysis (IGA) and thermogravimetric analysis (TGA), respectively. Isothermal aging studies for the monomers were carried out at 600°F (316°C), 650°F (343°C) and 700°F (371°C) were maintained. All samples were cured under N<sub>2</sub> atmosphere at 250–256°C for 8 hours and allowed to cool to room temperature under nitrogen atmosphere. The results are displayed in Table 1 and Table 2. A representative DSC thermogram is shown in Figure 1.

### Scheme III



In general, all three monomers possess sufficiently wide processing windows, 101–106°C. Polymerization exotherms begin at 229–250°C and reach their maxima at 258–263°C. We observed some very minor decompositions, especially with the polymer bearing the sulfone moiety in the backbone. In any event, the cured samples of all three bisbenzocyclobutene imide monomers were surprisingly stable toward thermooxidative degradation; only 17-percent weight

loss was observed after 200 hrs in 600°F (316°C) environment. The most thermoxidatively resistant resin suffers a mere 13-percent weight loss at 650°F (343°C) and 40-percent weight loss at 700°F (371°C) (see Figure 2 and Table 1). It is clear from the IGA results that the skeleton with the most structural rigidity is also the most heat-tolerant. Hence, the increasing order of thermoxidative stabilities are:



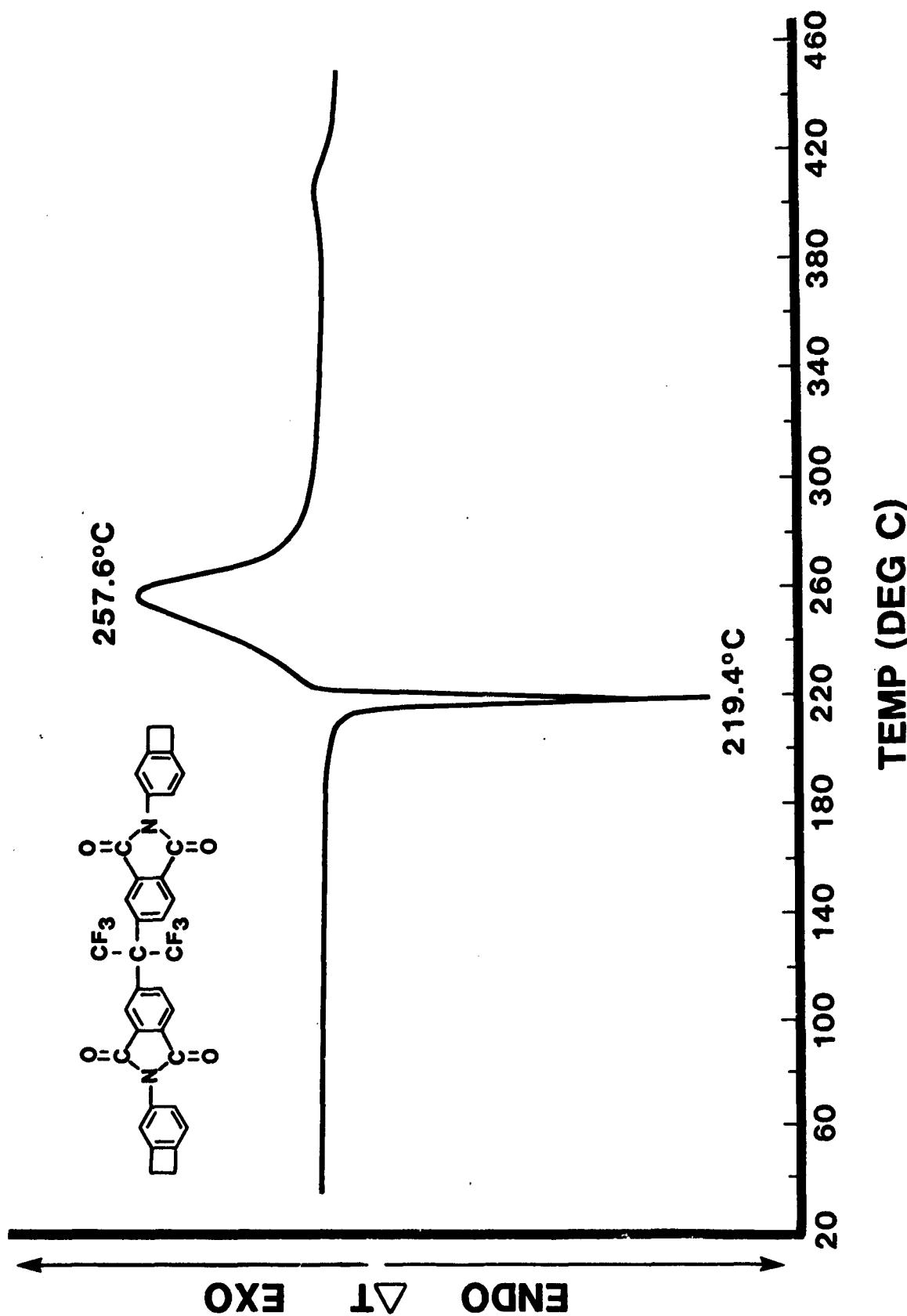
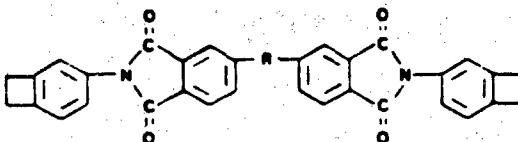


Figure 1. DSC Thermogram of bis-2,2-(N-4-benzocyclobutenyl phthalimido) hexafluoropropane (7a)

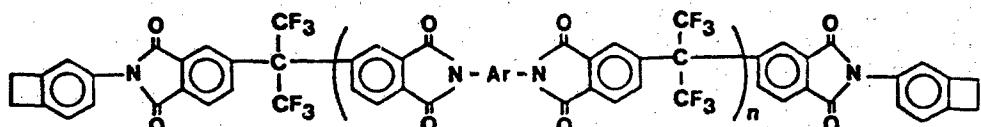
Table 1: THERMAL PROPERTIES<sup>a</sup>



R	T <sub>g</sub>	T <sub>m</sub>	T <sub>poly</sub> ONSET MAX	T <sub>g</sub> (CURE) DSC <sup>b</sup>	ISOTHERMAL AGEING 200 HRS. AIR % WEIGHT LOSS
-CF <sub>3</sub> -C-CF <sub>3</sub>	116	219	230 258 404 <sup>c</sup>	261	9% (600°F) 13% (650°F) 40% (700°F)
-O-C(=O)-O-C(=O)-O-	62		229 263 369 <sup>c</sup>	247 (251) <sup>d</sup>	7% (600°F) 25% (650°F)
-O-C(=O)-S-C(=O)-O-	149	249	250 263 357 377 <sup>c</sup>	240	10% (600°F)

NOTE: (a) ALL NUMERICAL VALUES ARE EXPRESSED IN °C. DSC WAS RUN AT HEATING RATE 20°C MIN. (b) MEASUREMENTS WERE MADE ON SAMPLES PREVIOUSLY CURED UNDER N<sub>2</sub> ATMOSPHERE AT 250°-254°C FOR 8 HOURS. (c) SMALL SECONDARY EXOTHERMS WITH PEAK VALUES AS INDICATED: OBSERVED FOR BOTH UNCURED AND CURED SAMPLES (d) DETERMINED BY THERMAL MECHANICAL ANALYSIS.

Table 2: THERMAL CHARACTERISTICS<sup>a</sup>

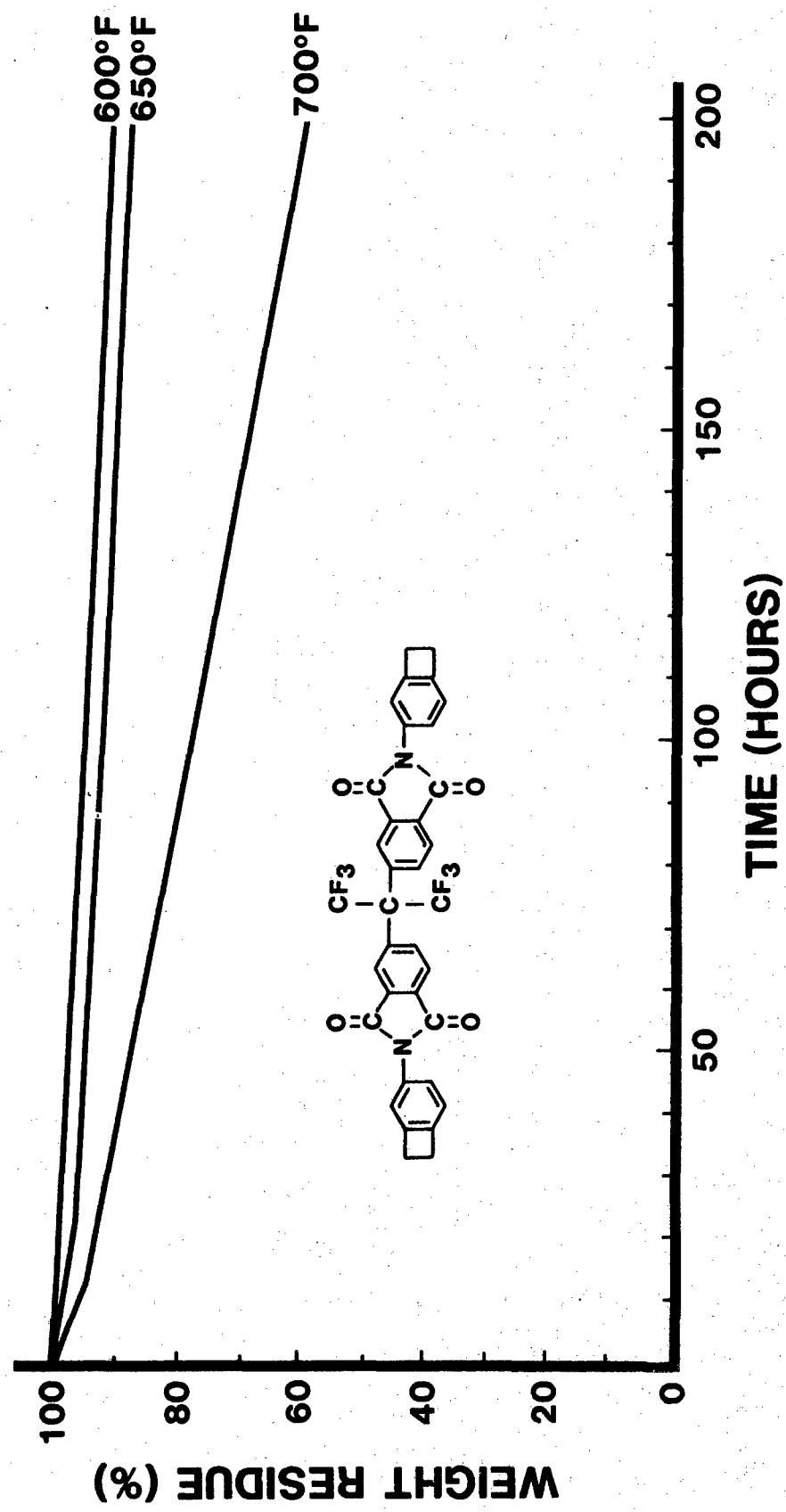


Ar	T <sub>g</sub>	T <sub>m</sub>	CURING <sup>b</sup> EXOTHERM ONSET MAX.	T <sub>g</sub> (cure) <sup>c</sup>	T <sub>10%</sub> <sup>d</sup>	%WEIGHT LOSS ISOTHERMAL 200HR, AIR
n=O	116°	219°	232° 258°	281° <sup>e</sup> (DSC)	496°	13% (650°F) 43% (700°F)
	~81°	-	197° 257°	258° <sup>e</sup> 256° (DSC)	470°	12% (650°F) 43% (700°F)
	~81°	-	210° 254°	288° <sup>e</sup> 314°(TMA) <sup>e</sup> 299°(DSC) <sup>e</sup>	500°	12% (650°F) 24% (700°F)
	~78°	-	208° 254°	289°(DSC) <sup>e</sup>	519°	13% (650°F) 35% (700°F)
	~81°	-	213° 252°	282°(DSC) <sup>e</sup>	518°	17% (650°F) 41% (700°F)

NOTES:

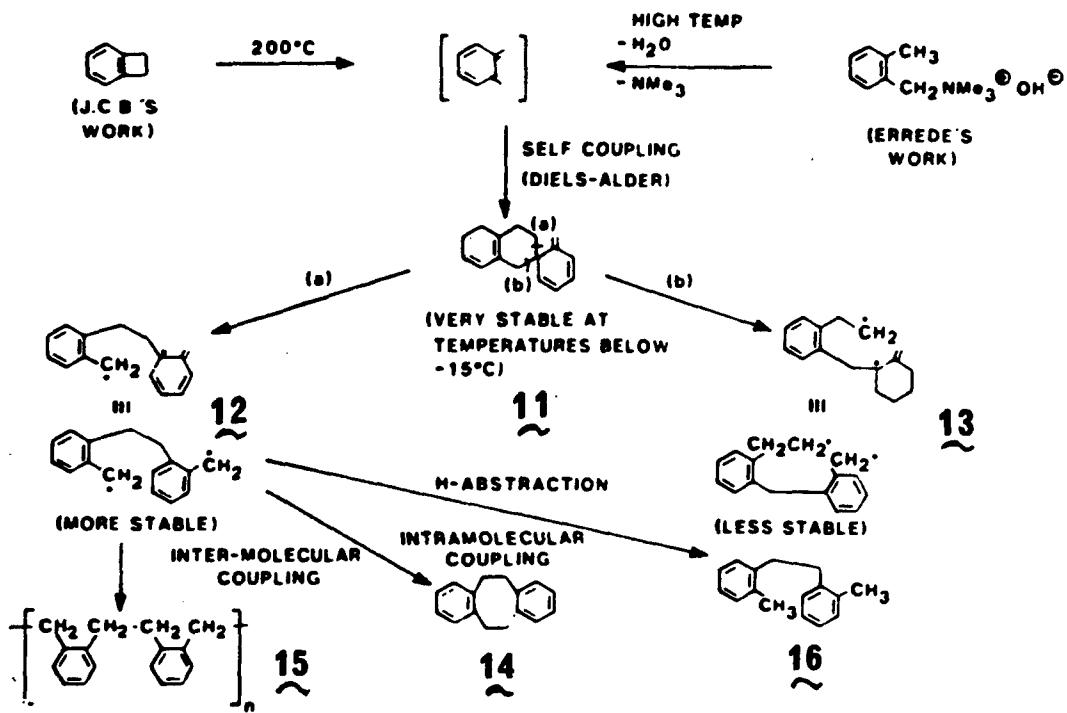
(a) ALL TEMPERATURE VALUES ARE EXPRESSED IN °C UNLESS OTHERWISE SPECIFIED. (b) SMALL EXOTHERMS AROUND 360°-380°C WERE ALSO OBSERVED. (c) UNLESS OTHERWISE SPECIFIED, VALUES WERE OBTAINED BY RESCANNING THE SAMPLES PREVIOUSLY HEATED TO 450°C ON DSC. (d) TEMPERATURE AT WHICH 10% WEIGHT LOSS OF THE SAMPLE OBSERVED BY TGA. (e) SAMPLES WERE PREVIOUSLY CURED AT 250°C/8HR/N<sub>2</sub>.

To address the question of the observed unusual thermooxidative stabilities of the bisbenzocyclobutene-based aromatic imide thermosets, the information concerning the molecular structures inherent in the polymeric materials is required. Even better if facts related to the reaction mechanisms, from which the polymeric structures arise, are known. Unfortunately, the exact cure mechanism for the bisbenzocyclobutene systems is still not clear. However, sufficient fundamental work has been done on the thermal behavior of benzocyclobutene, and we can make some inferences and hypothesis concerning the cure pathway and cured state of bisbenzocyclobutene systems. Scheme IV outlines our proposed reaction mechanism of benzocyclobutene based primarily on the results from the studies of Jensen's group<sup>16</sup> and Errede<sup>17</sup> on the thermal chemistry of benzocyclobutene and a precursor of its more reactive valence-isomer, o-xylylene.



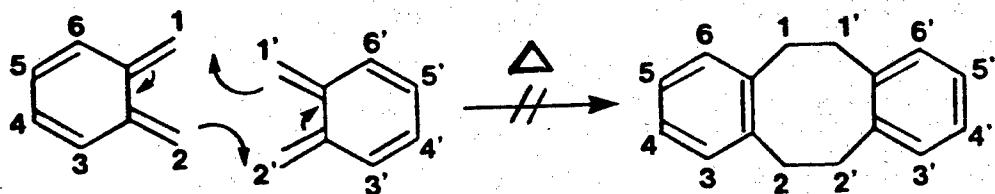
**Figure 2: ISOTHERMAL AGEING**

Scheme IV

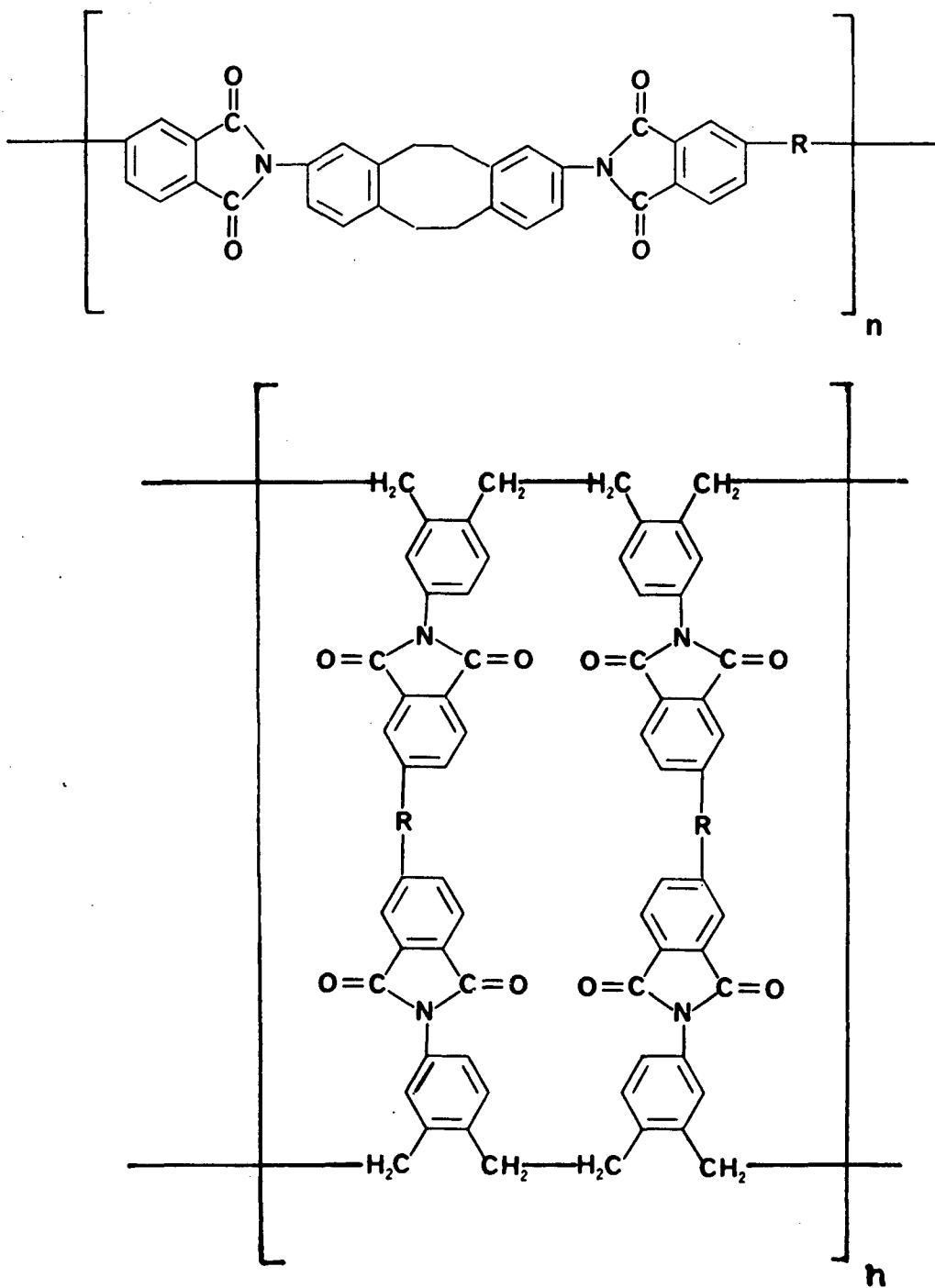


In brevity, benzocyclobutene undergoes an electrocyclic ring-opening to form the highly reactive o-xylylene, which can function as both a diene and a dienophile, a case that is reminiscent of cyclopentadiene. The self-reaction of o-xylylene via a Diels-Alder cycloaddition will lead to the formation of the spiro-intermediate 11 which is reported to be very stable at temperatures below  $-15^{\circ}\text{C}$ . On account of the strains at the spiro junction, 11 can rupture homolytically either at bond (a) or bond (b), which exhibit bond strains. However, we believe that the bond-breaking process is more likely to occur at bond (a) than bond (b) because the former will generate a more stable diradical 12, which should eventually form the three final products 14, 15,

and 16. When the thermal generation of o-xylylene was conducted devoid of solvent, the products dibenzocyclo-octa-1,5-diene 14 and poly(o-xylylene) 15 have been isolated.<sup>17</sup> Furthermore, the proposed mechanism which is actually a combination of a concerted step and a radical pathway does explain the formation of dibenzocyclo-octa-1,5-diene 14 whose formation via a thermal [4π + 4π] cycloaddition mechanism is formally forbidden by the theory of Conservation of Orbital Symmetry<sup>18</sup>.



In an attempt to rationalize the cure mechanism of the bisbenzocyclobutene systems in the light of the thermal behavior of the parent benzocyclobutene, we see that there are at least two possible pathways for polymerization, namely, (1) cycloaddition and (2) linear addition<sup>19</sup>. In the cycloaddition mode, an eight-membered ring will be formed and incorporated into the highly aromatic skeleton. However, in the linear addition mode, a polymeric structure with a double strand of poly(o-xylylene) bridged by the aromatic imide groups can result. The structural representations of the polymers are depicted in Figure 3. We are inclined to believe that the first structure is the most likely one, based on the thermal (TGA) and thermoxidative (IGA) stability data because of the following reasoning. First, with the eight-membered ring fused to an aromatic system on each side, there is a possibility that the bridging ethylene groups can be easily oxidized to a fused octa-tetraene. The resultant conjugated system may then rearrange to a more thermodynamically stable structure under the



**Figure 3:** The structural representations of the thermosetting polymers derived from the solid state homopolymerization of benzocyclobutene-based starting materials.

high thermal conditions of cure. Attempts have been made to detect the generation of  $H_2$  during such oxidation process by the thermogravimetric analysis/mass-spectroscopy (TGA/MS). Unfortunately, both uncured and cured samples of 7a did not appear to evolve hydrogen gas under TGA/MS conditions. Water and a mixture of methylaniline and dimethylaniline were detected at approximately 480°C, and  $CF_3H$  and HF, at 540°C from the cured sample.

The second explanation for the unusual thermoxidative stability of the bisbenzocyclobutene systems will invoke the fact ladder polymers have remarkable stability toward thermoxidative degradation because of their double-standard (ladder-like) structures. An alicyclic structure can also be qualified for a ladder-like structure and homolytic cleavage of the weakest bond in the ring will not fragment the overall structure. Homolytic rupture and healing of this particular bond will continue until at higher temperature, a second bond in the alicyclic structure is also broken. Although we cannot offer it as a third reason, due to insufficient comprehension of the mechanism, we do feel that the cross-linking in the bisbenzocyclobutene systems must also play an important role in stabilizing them against thermoxidative degradation.

As supported by TGA/MS results, the weakest link in the polymeric structure is expectedly the aliphatic bridges of the eight-membered ring (structure 1) or the double ethylene strands (structure 2) which are, in fact, the proposed structures for the cure-site. Therefore, to improve on the  $T_g$ (cure) and the thermoxidative stability of the bisbenzocyclobutene systems. We are currently exploring two approaches: (1) dilution of the cure-site density with suitable chain-extending groups; (2) structural modification at the cure-site. We have completed the first approach by using a variety of commercially available aromatic amines. The selection of these

amines are based on their projected effects on the initial and final Tg's.

As evident from Table 2, all the bisbenzocyclobutene oligomers exhibit good flow characteristics, with broad initial Tg's, centered around 78°-81°C. The broadness of Tg's is due to the multi-component nature of the oligomers. Apparently, their flow characteristics also facilitate the polymerization process at indicated by lower onset temperatures (197°-213°C vs 232°C for the monomer, n=0). Furthermore, all but one cured materials derived from the oligomers have higher final Tg's and thermoxidative stability (700°F) than that derived from the monomer, (n=0), 7a. The thermoset, based on 10c, is less heat-resistant than that derived from 10b despite the fact that the former has the more rigid group, namely, the para-phenylene unit incorporated in the backbone structure than the latter, which has the meta-phenylene moiety. In addition, the final glass-transition temperatures higher than the cure temperature (250°C) can be obtained from these bisbenzocyclobutene thermosetting systems, particularly the one based on 10b (meta-phenylene) which exhibits remarkably high final Tg (314°C as determined by TMA) and excellent thermo-oxidative stability (24-percent weight loss at 700°F/Air/200 hrs). Such high Tg is reminiscent of the polyimide co-polymer derived from the polycondensation of a mixture of 2,2-bis(4-phthalic dicarboxylato) hexafluoro propane (6FTA), para-phenylenediamine and meta-phenylenediamine (Tg 350°-370°C)<sup>20</sup>.

### SECTION III

#### CONCLUSION

Our study demonstrates that the molecular structures with 600-650°F (316-343°C) stability can be realized with the cure chemistry of bis-benzocyclobutene systems<sup>23</sup>. In addition, the fact that the glass-transition temperatures of the thermosetting materials formed from the oligomers (see Table 2) are invariably higher than the cure temperature (250°C), at which the homopolymerization of bis-benzocyclobutene is near its maximum, may indicate that the bis-o-xylylene generated from bis-benzocyclobutene are so reactive that curing process is highly efficient and occurs to high degree prior to vitrification. Furthermore, it is possible to raise the softening points as well as the thermoxidative stability of the bis-benzocyclobutene thermosetting systems by diluting the cure-site density with various aromatic amines as the chain-extending agents, of which meta-phenylenediamine is more effective. Lower onset temperatures for curing are also noted for the bisbenzocyclobutene oligomers. In conclusion, our research indicates that the bisbenzocyclobutene system provides a new addition polymerization reaction to generate remarkably heat-resistant structures.

## SECTION IV

### EXPERIMENTAL

The preparation of 4-aminobenzocyclobutene was performed according to procedures (with some modifications) described in the literature<sup>12-15</sup>. The dianhydrides, 2,2-bis[4-(3,4-dicarboxyphenoxy) phenyl] hexafluoropropane dianhydride (BFDA) and 1,4-bis(3,4-dicarboxyphenoxy) diphenylsulfone dianhydride (BSDA) were prepared according to methods described in the patent literature<sup>21-22</sup>. Meta-phenylenediamine was purified by washing it with reagent-grade acetone in a fritted filter funnel until white crystals were obtained. All other chemicals were obtained from commercial sources and used without further treatment.

#### Preparation of bis-2,2-(N-4-benzocyclobutenyl phthalimido) hexafluoropropane (7a)

A mixture of bis-2,2-(4-phthalic anhydrido) hexafluoropropane (4.00 g, 10.1 mmol) and 4-aminobenzocyclobutene (2.40 g, 20.1 mmol) freshly prepared from the catalytic hydrogenation of 4-nitrobenzocyclobutene, were gently refluxed in acetic acid (75 ml) under nitrogen atmosphere overnight. The resultant dark and homogeneous reaction mixture was allowed to cool to room temperature and poured into 300 ml of H<sub>2</sub>O. Immediately, precipitation of gray solids occurred, which could be extracted into ethyl ether (100 ml, then 3 x 50 ml). The ethereal extract was then washed with aqueous sodium carbonate and dried over magnesium sulfate. Subsequent removal of the solvent by rotary evaporation led to the isolation of about 5.5 g of crude dark brown product, which was subjected to the following chromatographic purification. The crude product was dissolved in about 20 ml of methylene chloride and added to a quartz column (internal diameter: 2.0 cm) containing about 120 g of silica gel and saturated with petroleum ether. Elution with

1:1 ether/petroleum ether resulted in the collection of light yellow solution as first fractions, which, at room temperature, gradually deposited light yellow needles. The product was collected, washed with petroleum ether and dried in an oven at 100°C for about an hour. Yield: 3.78 g (58.7 percent) mp = 216-216.5°C. Anal. Calc. for  $C_{35}H_{20}F_6N_2O_4$ : C, 65.02; H, 3.12; N, 4.33. Found: C, 65.07; H, 3.23; N, 4.18. Mass spectroscopy: m/e 646 ( $M^+$ ) 30.7 percent. Proton NMR ( $CDCl_3$ ): 3.26 (singlet, alicyclic protons): 7.07-7.30, 7.85-8.18 (complex, aromatic protons) (Figure 4). Ir (KBr pellet): 2968 w, 2925w (alicyclic C-H stretches); 1778 m, 1717 vs (imide group stretches); 1243<sub>s</sub>, 1188<sub>s</sub> (asymmetric and symmetric stretches of  $-C(CF_3)_2$ -group) (Figure 5).

Preparation of 2,2-bis[4-(N-4'-benzocyclobutenyl)-4"-phenoxyphthalimido] hexafluoropropane (7b)

A mixture of 1.63 g (13.7 mmol) of freshly prepared 4-amino-benzocyclobutene and 4.00 g (6.36 mmol) of 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl] hexafluoropropane dianhydride (BFDA) was heated to reflux in acetic acid (60 ml) under  $N_2$ . The reaction mixture became homogeneous and dark upon reflux, which was maintained for about 17 hours. The dark reaction mixture was allowed to cool to room temperature and poured into about 350 ml of distilled water. The mixture was then extracted using methylene chloride (100 ml, then 3 x 50 ml) as the extracting solvent. The organic extract was then washed with aqueous sodium carbonate and saturated sodium chloride solution, and finally dried over magnesium sulfate. The resultant solution was concentrated on a rotary evaporator until its volume was about 50 ml, and subjected to chromatographic purification, (350-g silica gel saturated with hexane; 1:1  $CH_2Cl_2$ /hexane as eluent). The desired product was obtained, after the removal of solvent from the first fractions, as light yellow microcrystalline solid. Yield: 3.74 g (67.8 percent), mp = 128-132°C.

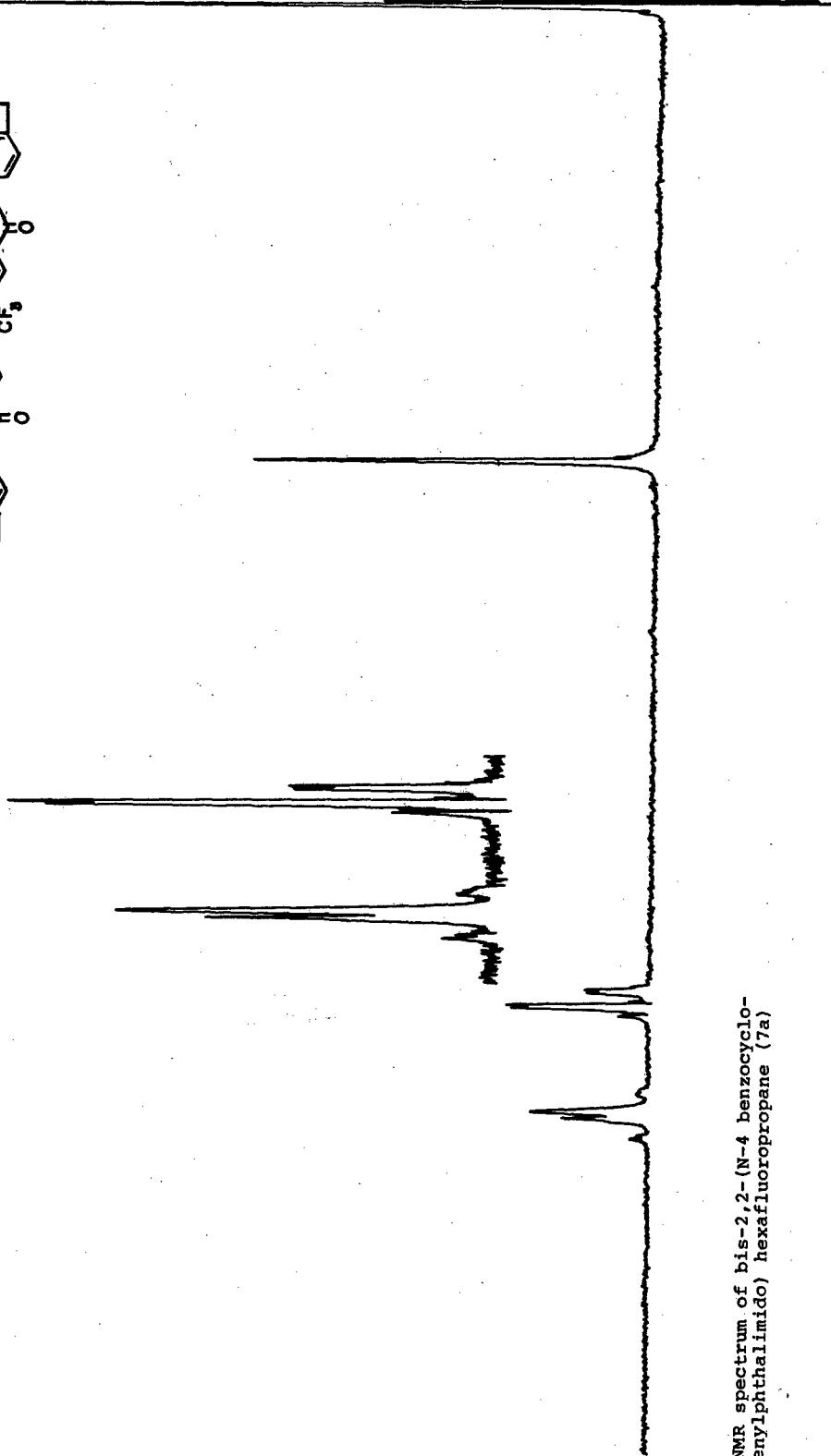
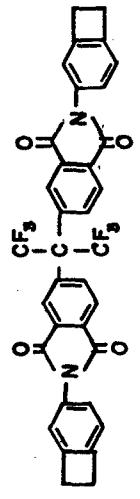


Figure 4.  $^1\text{H}$  NMR spectrum of bis-2,2-(N-4-benzocyclobutenylphthalimido) hexafluoropropane (7a)

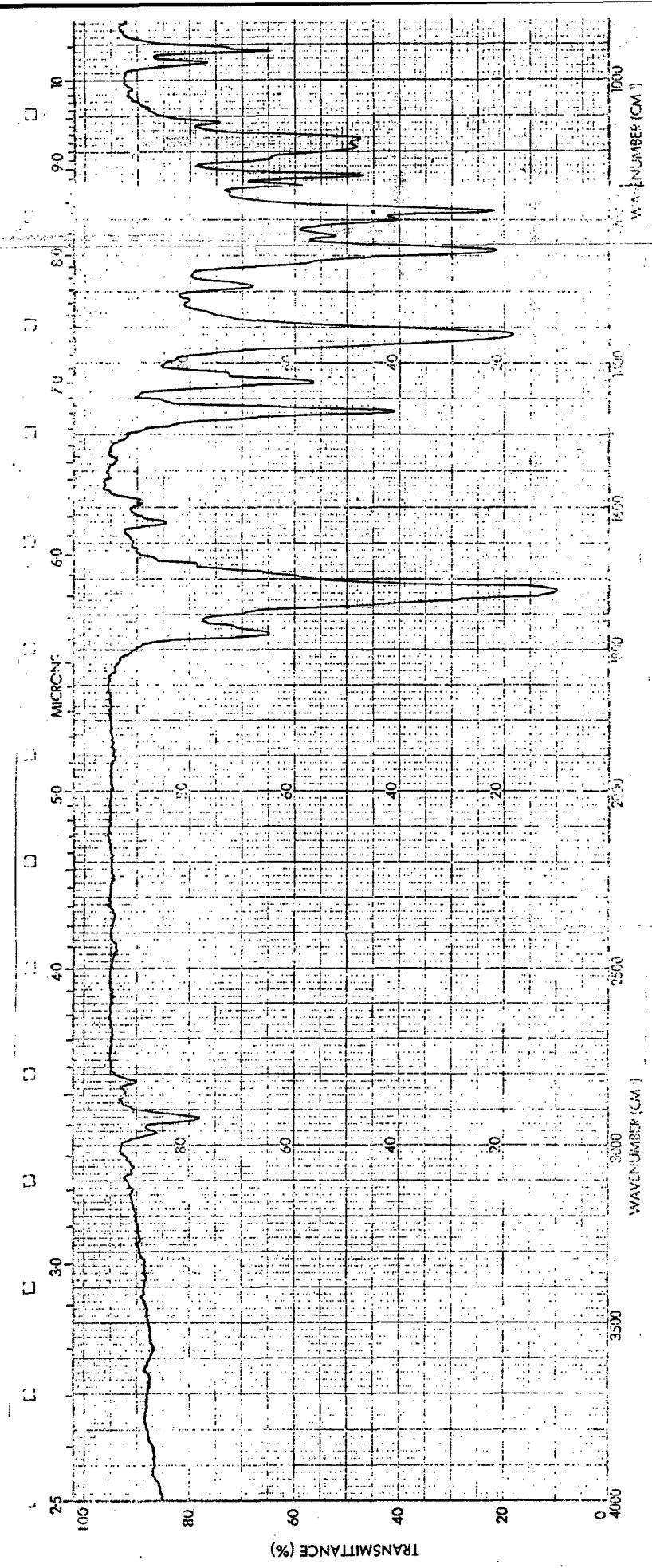
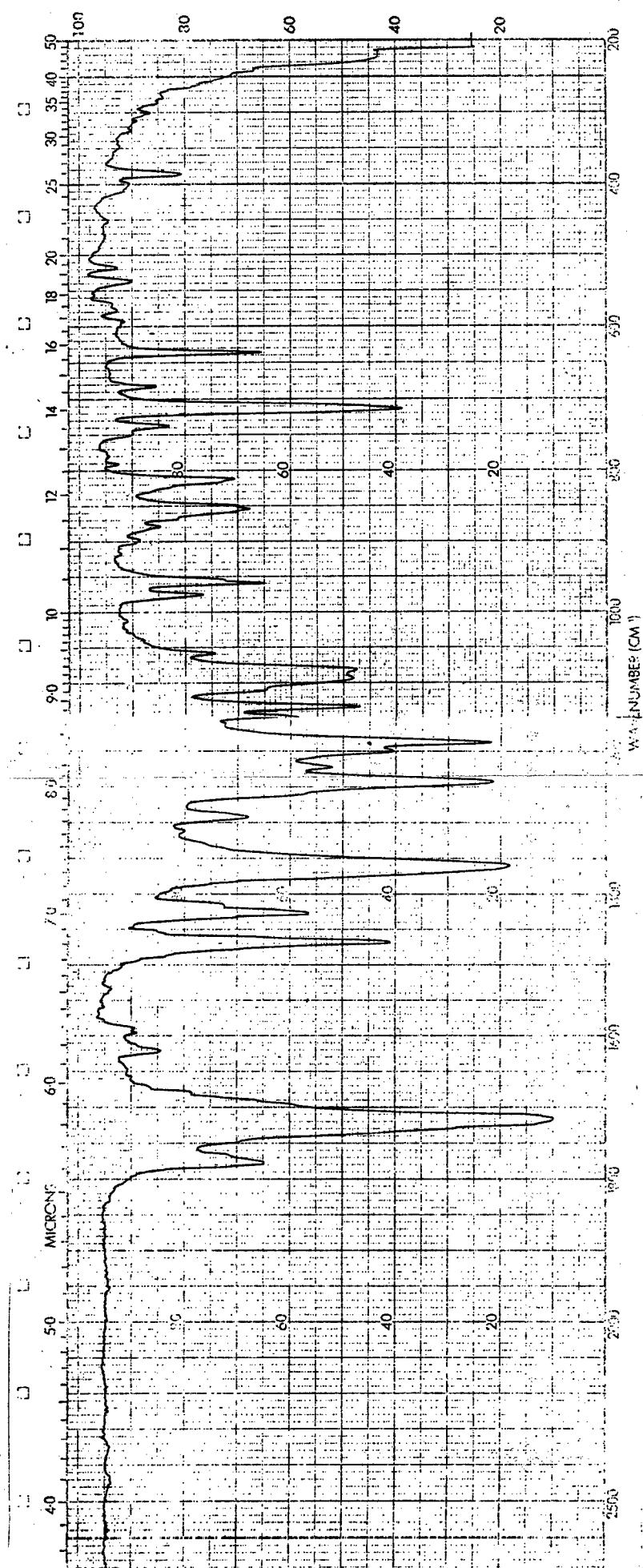


Figure 5. Infrared spectrum of bis-2,2-(N-4-benzocyclobutenyphthalimido)hexafluoropropane (7a)

10f2



thalimide

2 of 2

Anal. Calc. for  $C_{47}H_{28}F_6O_6N_2$ : C, 67.94; H, 3.40; N, 3.37. Found: C, 67.99; H, 3.76; N, 3.19. Mass spectroscopy: 830 ( $M^+$ , 2 percent); 415 ( $M^{++}$ , 6 percent). Proton NMR ( $CDCl_3$ ): 3.23 (singlet, alicyclic protons); 7.06-8.03 (complex, aromatic protons) (Figure 6). IR (KBr pellet); 2922 w, 2960 vw (alicyclic C-H stretches); 1714 vs, 1771 m (imide group stretches); 1201 m, 1235s (symmetric and asymmetric stretches of  $-(CCF_3)_2$ -group); 1168 ms (Ar-O-Ar stretch) (Figure 7).

Preparation of bis-[4-(N-4'-benzocyclobutenyl-4"-phenoxyphthalimido)] sulfone (7c)

A mixture of 4-aminobenzocyclobutene (0.75 g, 6.29 mmol) and 1,4-bis(3,4-dicarboxyphenoxy)diphenylsulfone dianhydride (1.50 g, 2.96 mmol) was refluxed in acetic acid (55 ml) under  $N_2$  overnight. The resultant dark reaction mixture was allowed to cool to room temperature and poured into 300 ml of distilled water. The crude product was then extracted into methylene chloride (100 ml, then 3 x 50 ml) and the organic extract was subsequently treated with 10-percent aqueous sodium bicarbonate and saturated sodium chloride solution. After drying over magnesium sulfate, the methylene chloride extract was concentrated on a rotary evaporator until its volume was about 35-40 ml. Subsequent chromatographic purification (300-g silica gel saturated with petroleum ether; 1:1 methylene chloride/petroleum ether as the eluting solution) led to the isolation of the desired product, which was obtained from the first fractions as light yellow microcrystalline solid.

Yield: 1.18 g (53.6 percent) mp = 245-246°C. Anal. Calc. for  $C_{44}H_{28}N_2O_8S$ . 70.96 percent; 3.79 percent H; 3.76 percent N. Found 70.81 percent C; 3.99 percent H; 3.64 percent N. Proton NMR ( $CDCl_3$ ): 3.25 (singlet, alicyclic protons); 7.09-7.54, 7.96-8.16 (complex; aromatic protons) (Figure 8). IR (KBr pellet): 3060 vw, 3085 vw (aromatic C-H stretches); 2930 w, 2965 vw

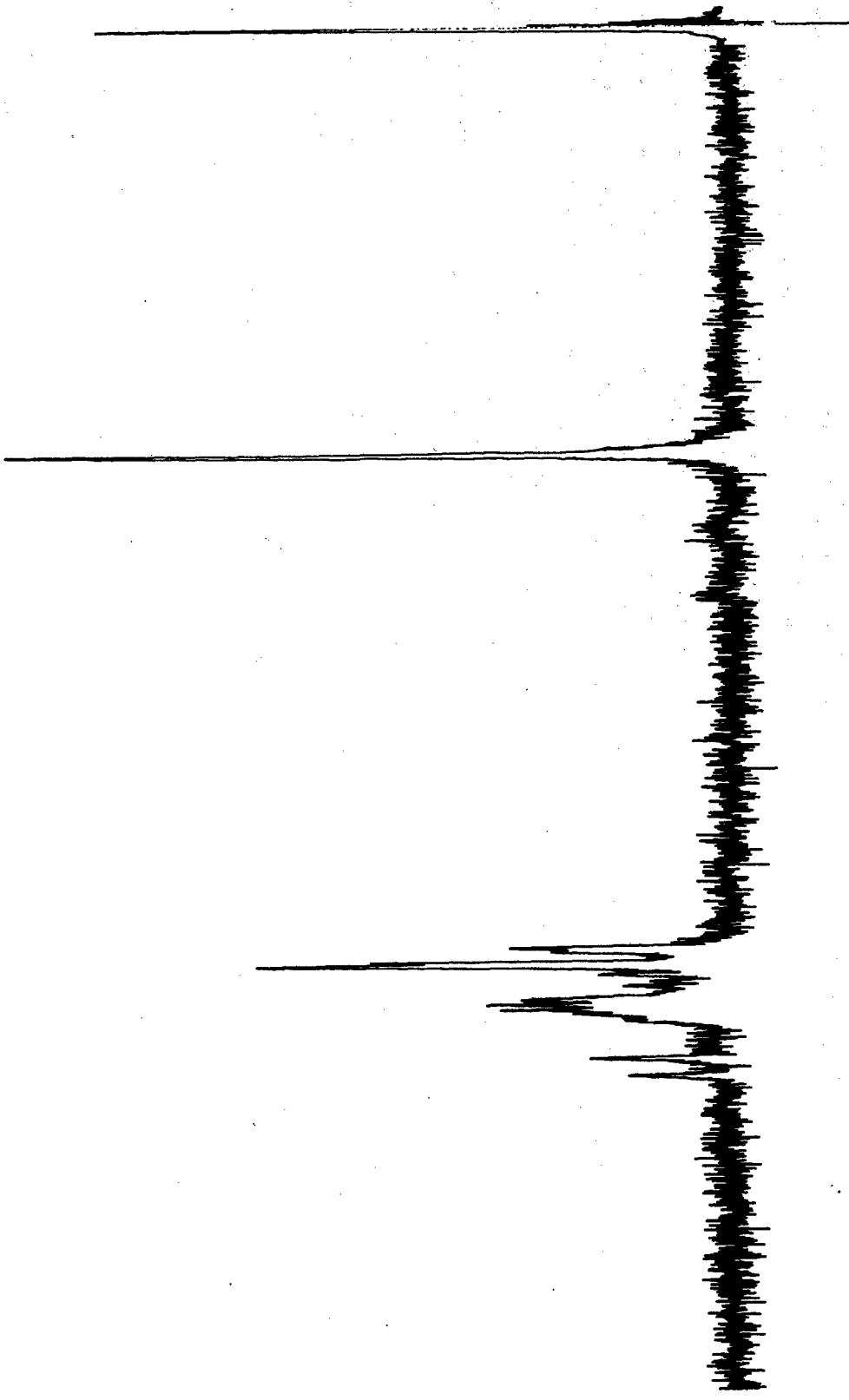


Figure 6.  $^1\text{H}$  NMR spectrum of 2,2-bis[4-(N-4'-benzocyclobutenyl)-4"-phenoxyphthalimido] hexafluoropropane (7b)

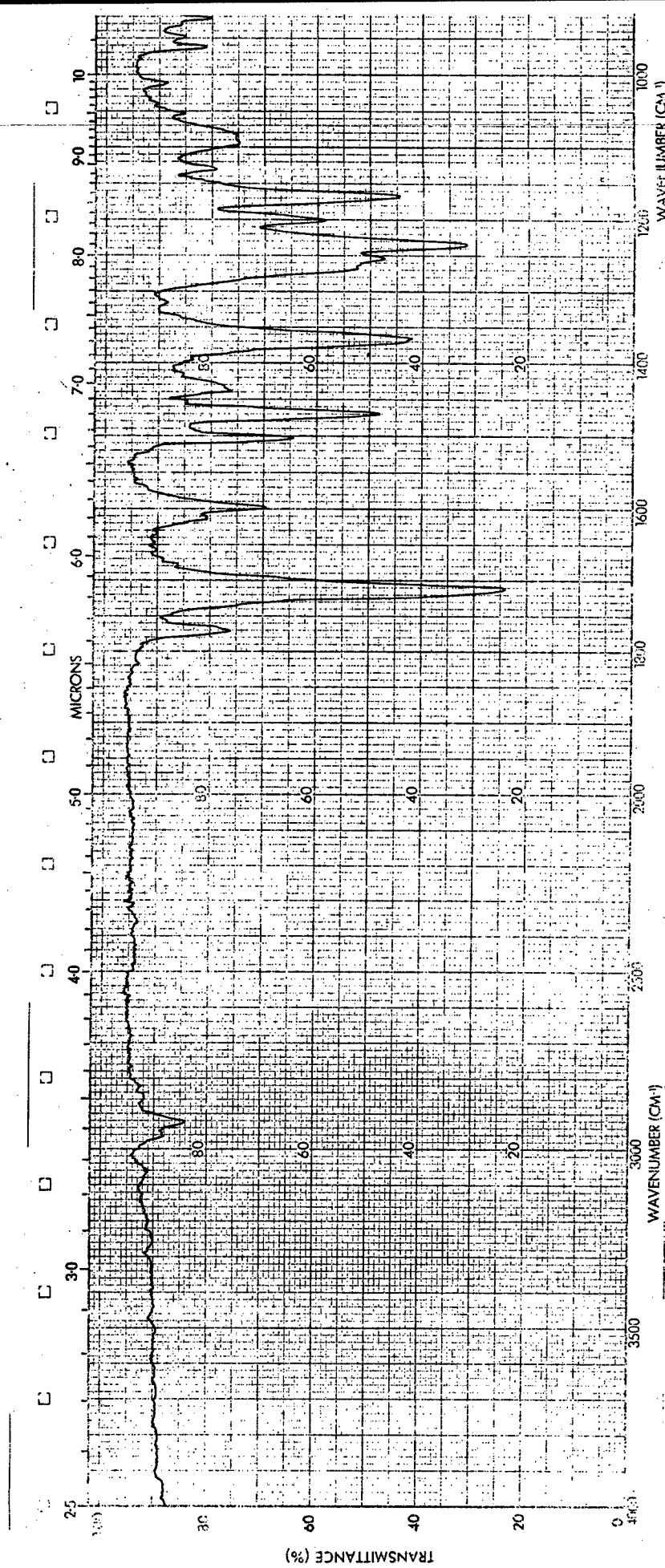
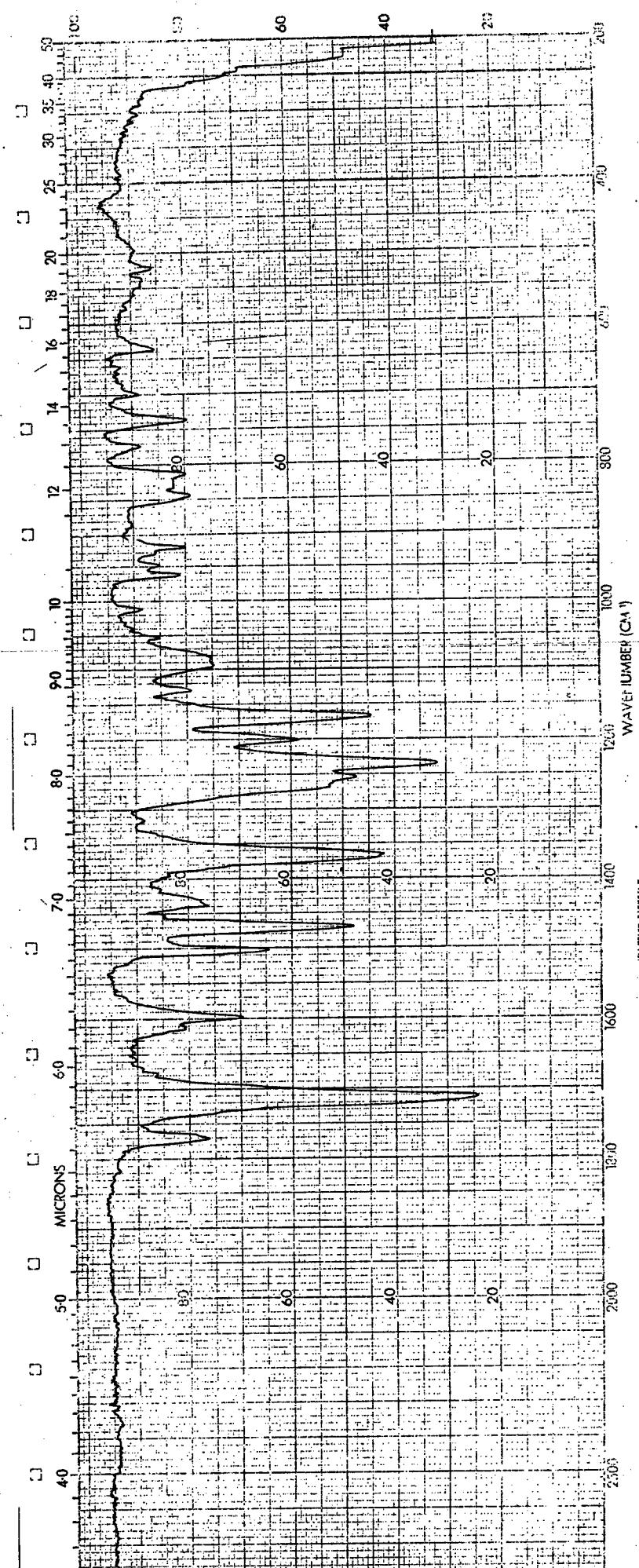


Figure 7. Infrared spectrum of 2,2-bis[4-(N-4'-benzoylclobutenyl-4"-phenoxyphthalimido)] hexafluoropropane-(7b)

1 of 2



utetyl-4"

20f2

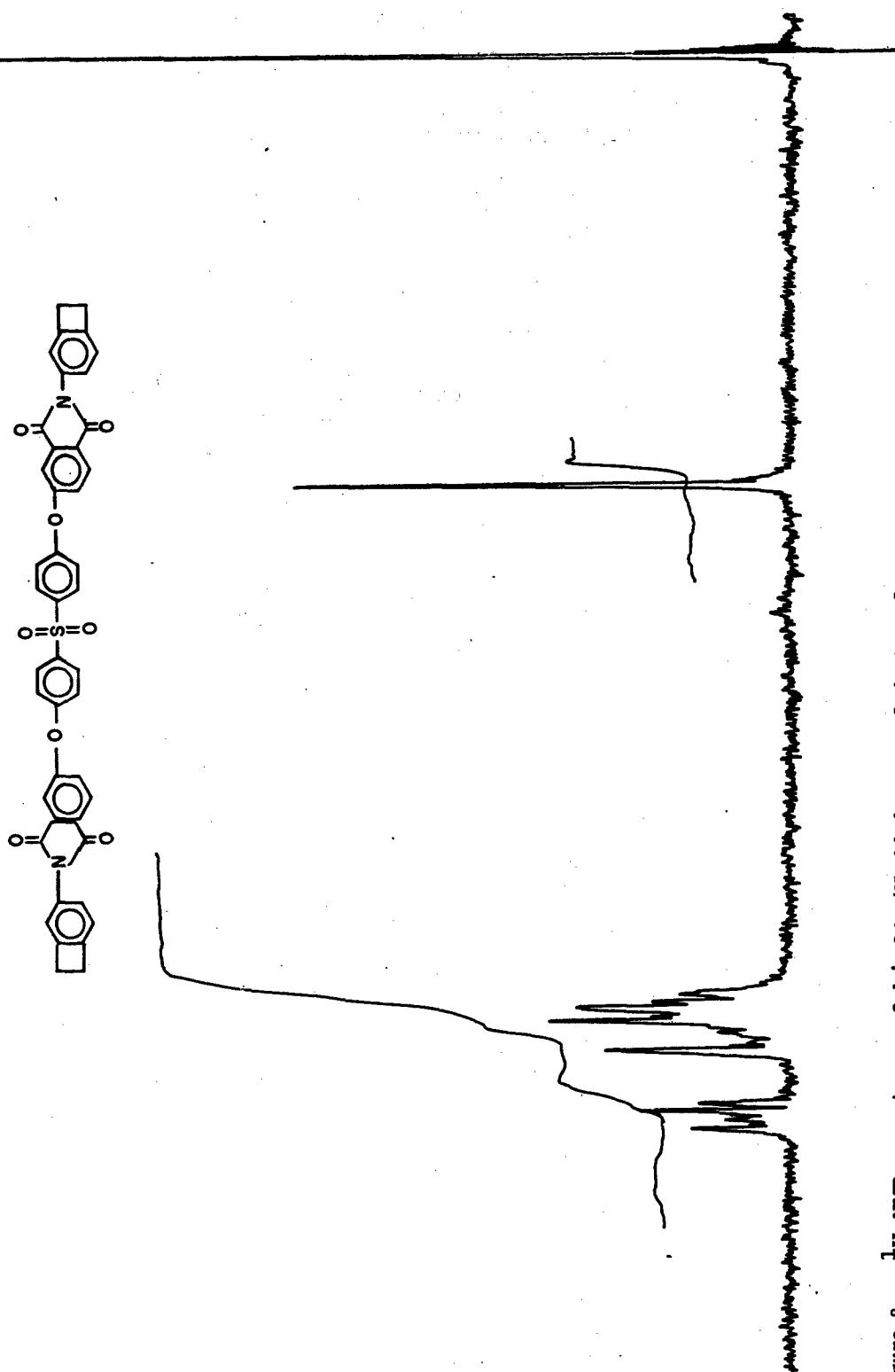


Figure 8.  $^1\text{H}$  NMR spectrum of bis[4-(N-4'-benzocycllobutenylidio)-4''-phenoxyphthalimido] sulfone (7c)

(alicyclic C-H stretches); 1700 vs; 1764 ms (imide group stretches); 1232 (symmetric and asymmetric stretches of  $-SO_2-$ group); 1089, 1102 ms (Ar-O-Ar stretches) (Figure 9).

Preparation of oligomeric mixture 10a

3.79 (8.53 mmol) of bis-2,2-(4-phthalic anhydido) hexafluoropropane, 0.45 g (4.16 mmol) of m-phenylenediamine (purified by washing it with acetone in a fritted filter funnel until white crystals were obtained) and 1.10 g (9.23 mmol) of 4-aminobenzocyclobutene was reacted in 120-ml acetic acid/60-ml toluene at 110°C as described above. After the usual work-up, the crude product was dissolved in about 100 ml of methylene chloride and filtered through a bed of silica gel (50 g) on a fritted filtered funnel, washing with methylene chloride until the filtrate was almost colorless. Removal of the solvent from the yellow filtrated led to the isolation of the desired product as a light tan microcrystalline solid. Yield: 3.20 g.  $^1H$  NMR (Figure 10) IR(KBr) (Figure 11).

Preparation of Oligomeric mixture 10b

5.75 g (12.94 mmol) of bis-2,2-(4-phthalic anhydido) hexafluoropropane 0.80 g (7.40 mmol) of p-phenylenediamine and 3.60 g (30.21 mmol) of 4-aminobenzocyclobutene were reacted in 200-ml acetic acid/100-ml toluene. The crude product was dissolved in about 30 ml of methylene chloride and the resultant solution was passed through a small column containing 50 g of silica gel saturated with petroleum ether, which was also used as the eluting solvent. The desired product was a golden microcrystalline solid. Yield: 4.60 g. Analysis by HPLC indicated the following oligomeric composition n = 0, 47.9 percent; n = 1, 44.9 percent; n = 2, 6.9 percent.  $^1H$  NMR (Figure 12), IR(KBr) (Figure 13).

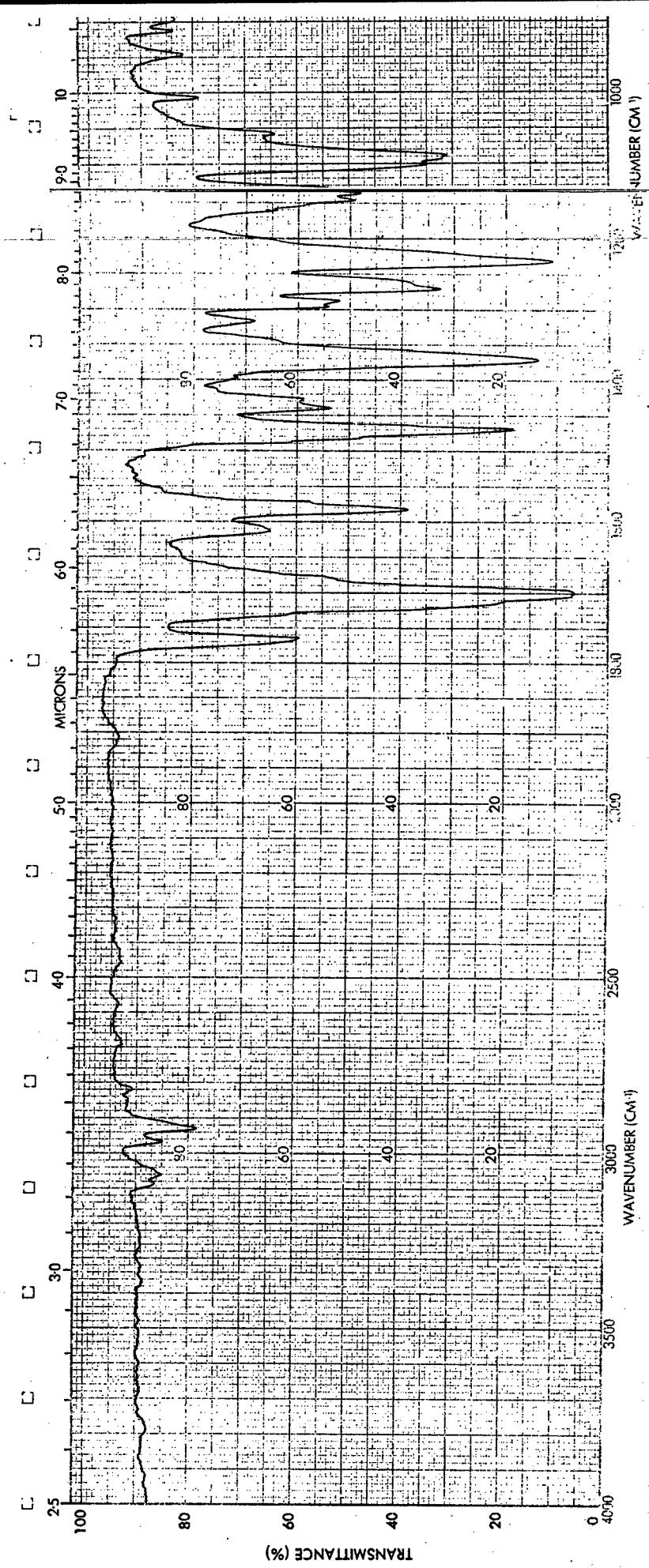
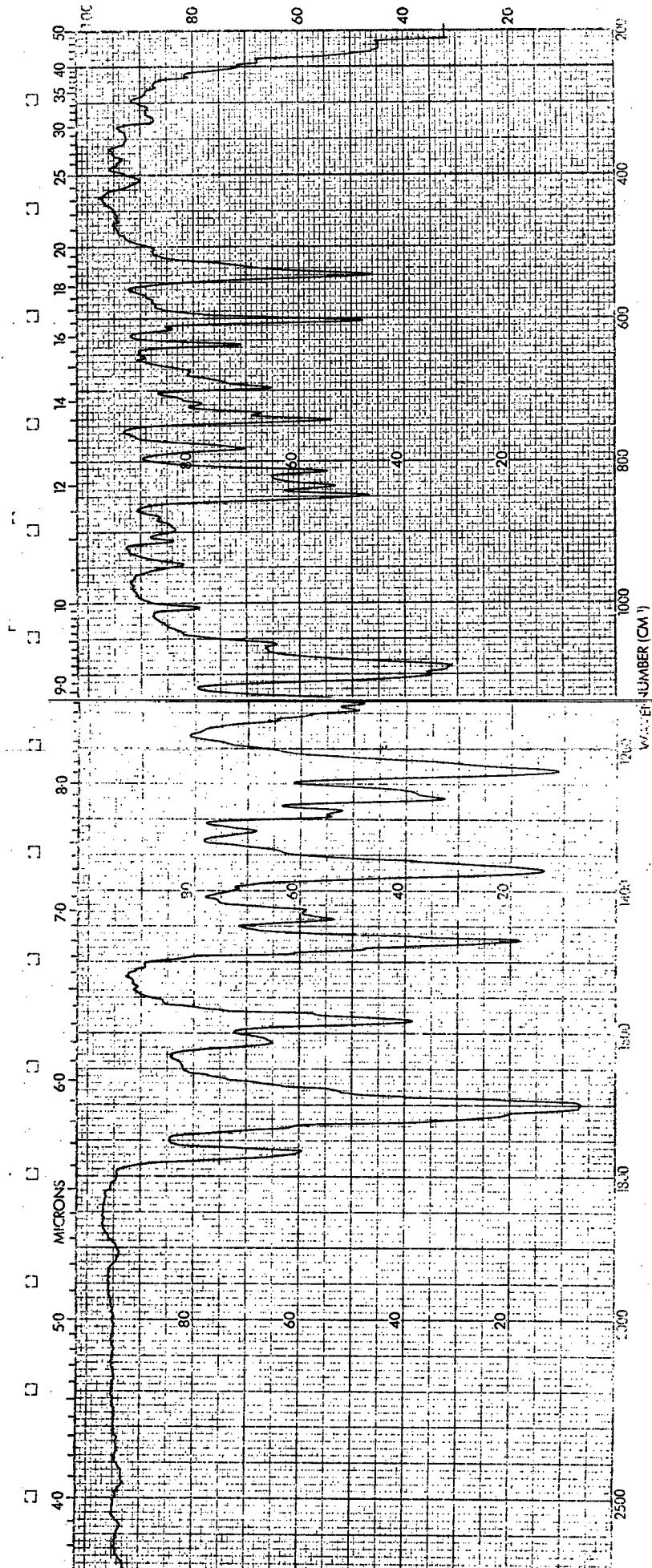


Figure 9. Infrared spectrum of bis[4-(N-4-benzocyclobutenyl-4'-phenoxyphthalimido)] sulfone (7c)

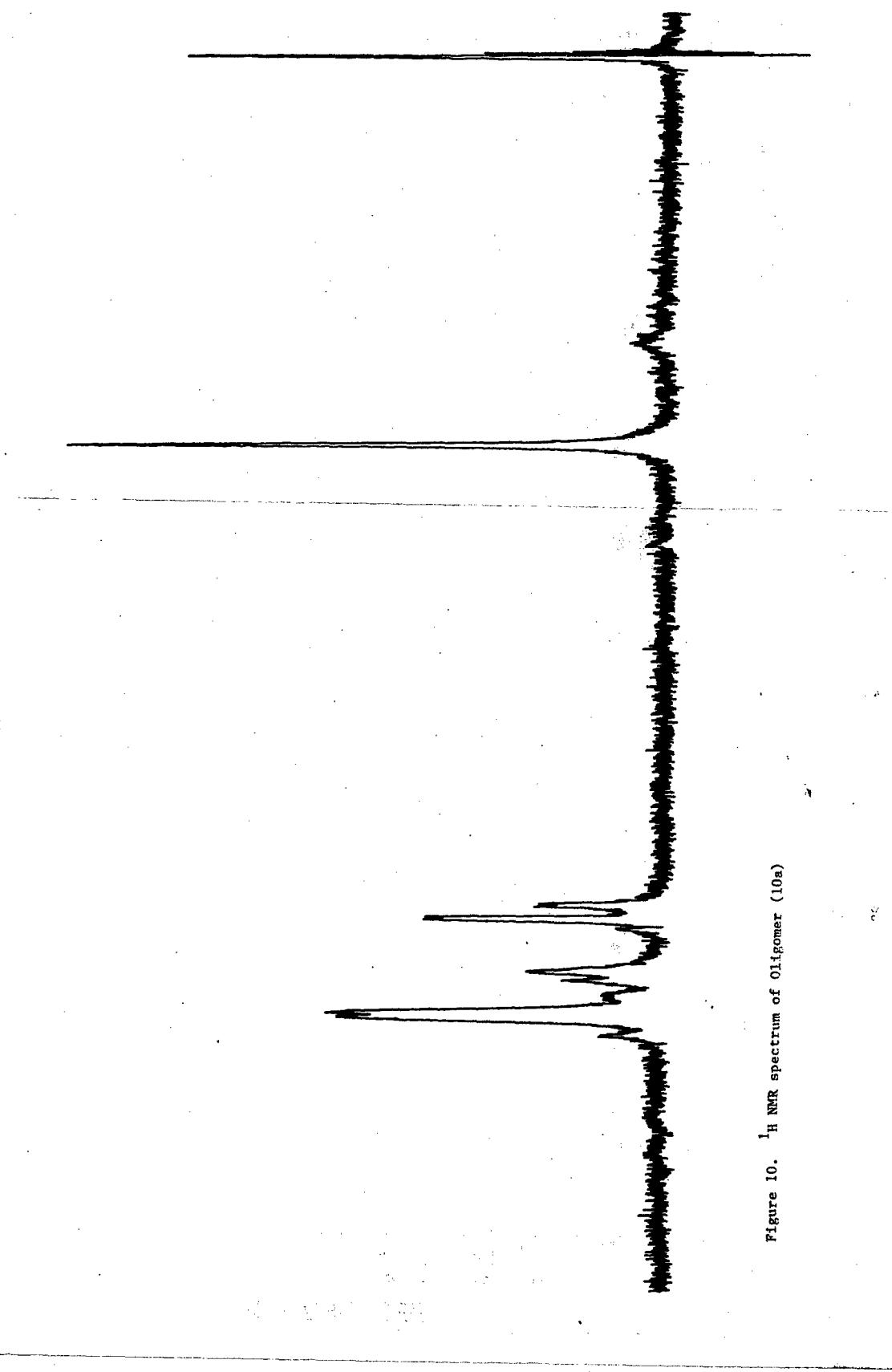
1 of 2



y1=4"

20f2

Figure 10.  $^1\text{H}$  NMR spectrum of Oligomer (10a)



**BECKMAN**

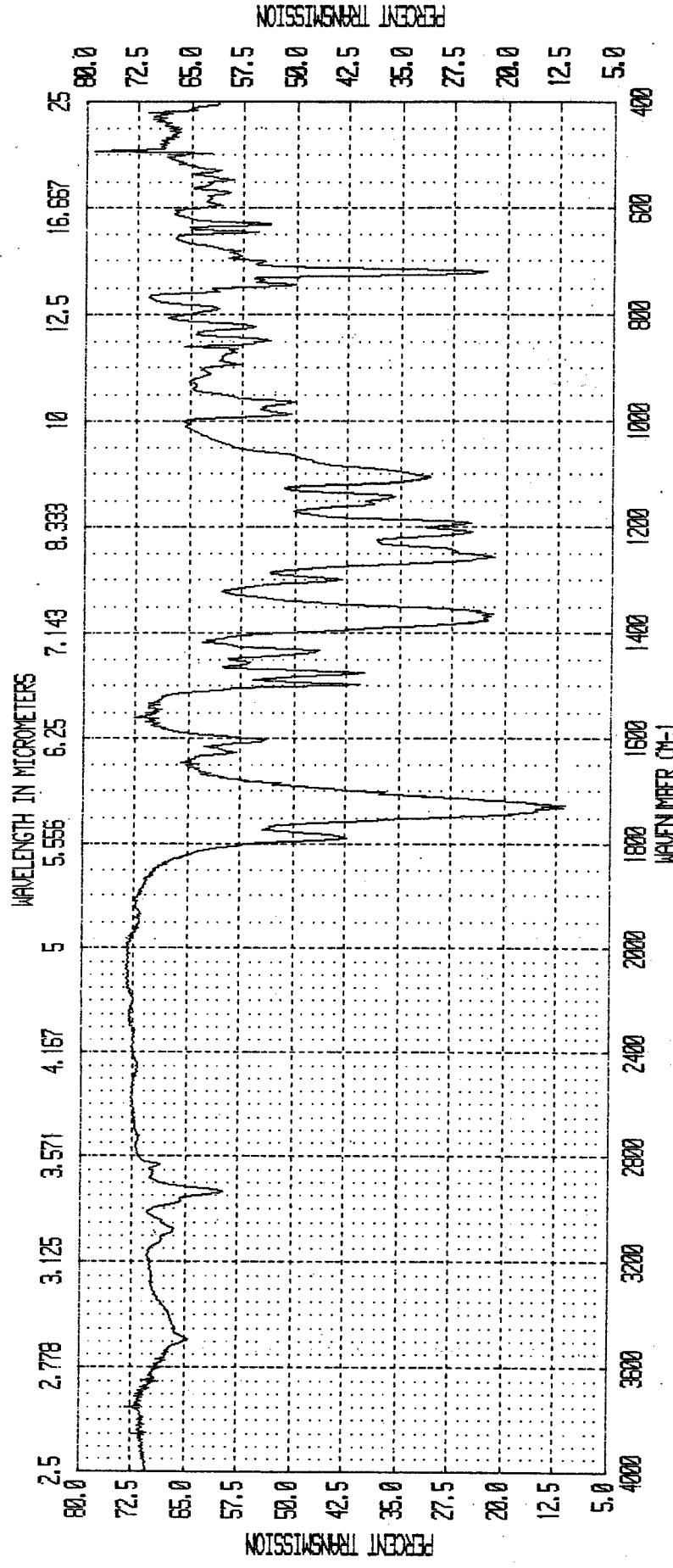


Figure 11. Infrared spectrum of oligomer (10a)

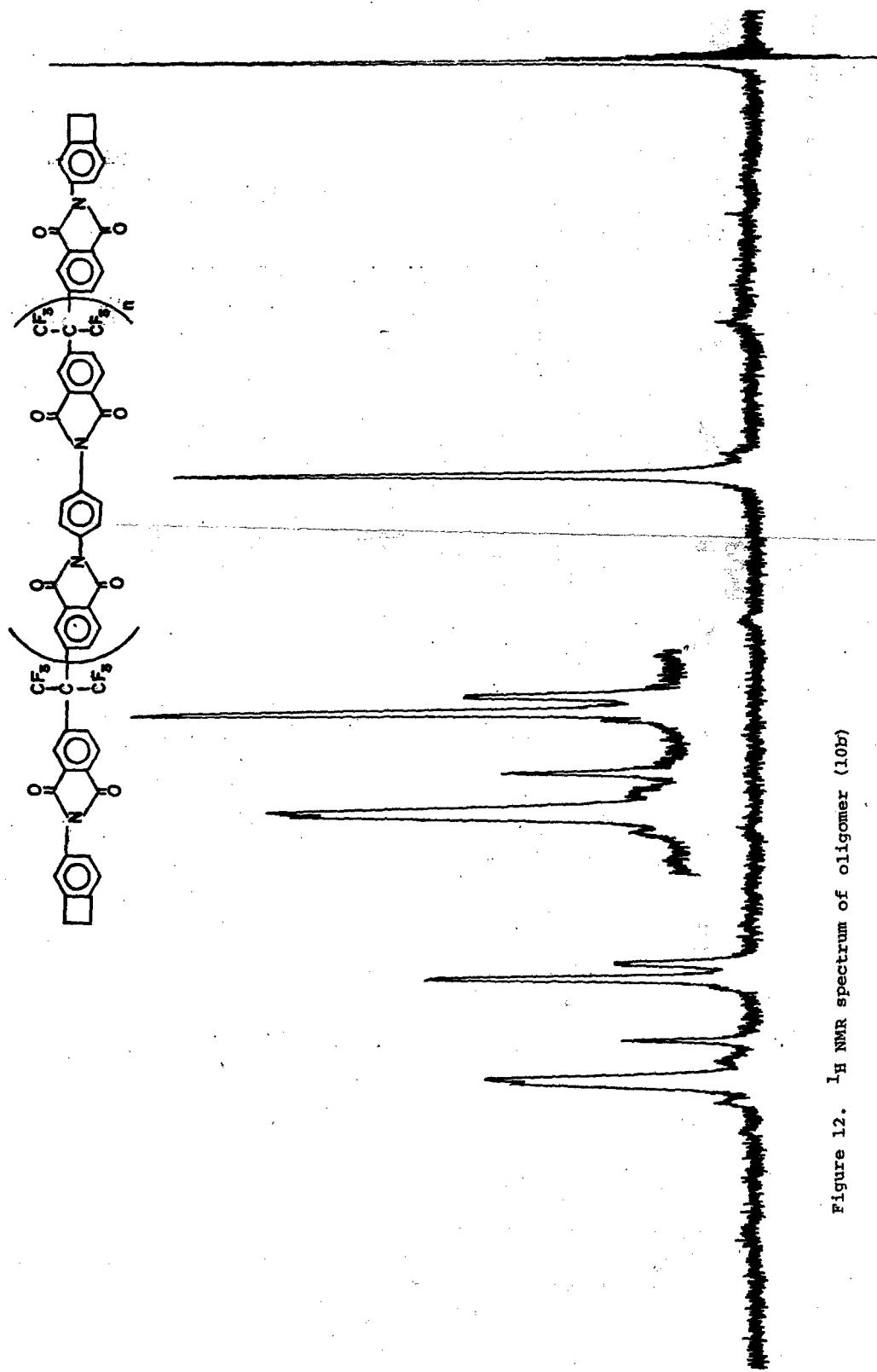


Figure 12.  $^1\text{H}$  NMR spectrum of oligomer (10b)

**BECKMAN**

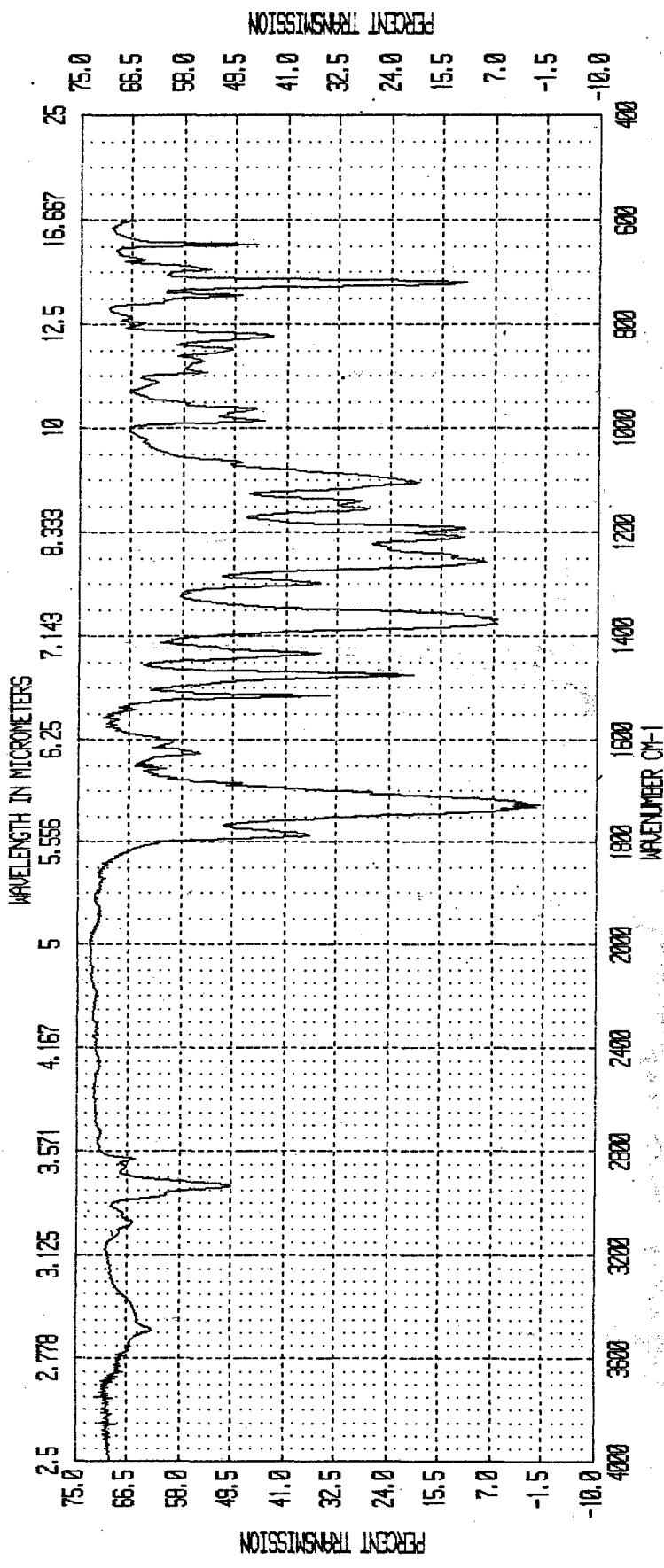


Figure 13. Infrared spectrum of oligomer (106)

Preparation oligomeric mixture 10c

5.75 g (12.94 mmol) of bis-2,2-(4-phthalic anhydrido) hexafluoropropane, 1.30 g (6.49 mmol) of oxydianiline and 3.70 g (31.0 mmol) of 4-aminobenzocyclobutene were reacted in 200-ml acetic acid/100-ml toluene. The crude product was dissolved in -110-ml methylene chloride, after the usual work-up as described above. The resultant solution was then passed through a small column containing about 50-g silica gel, using hexane as the eluting solvent. The desired product was obtained from the first fractions as amber microcrystalline solid. Yield: 6.40 g. Analysis by HPLC indicated the following oligomeric composition:  $n = 0$ , 31.6 percent;  $n = 1$ , 29.9 percent;  $n = 2$ , 19.4 percent;  $n = 3$ , 10.9 percent;  $n = 4$ , 7.4 percent.  $^1H$  NMR (Figure 14), IR(KBr) (Figure 15).

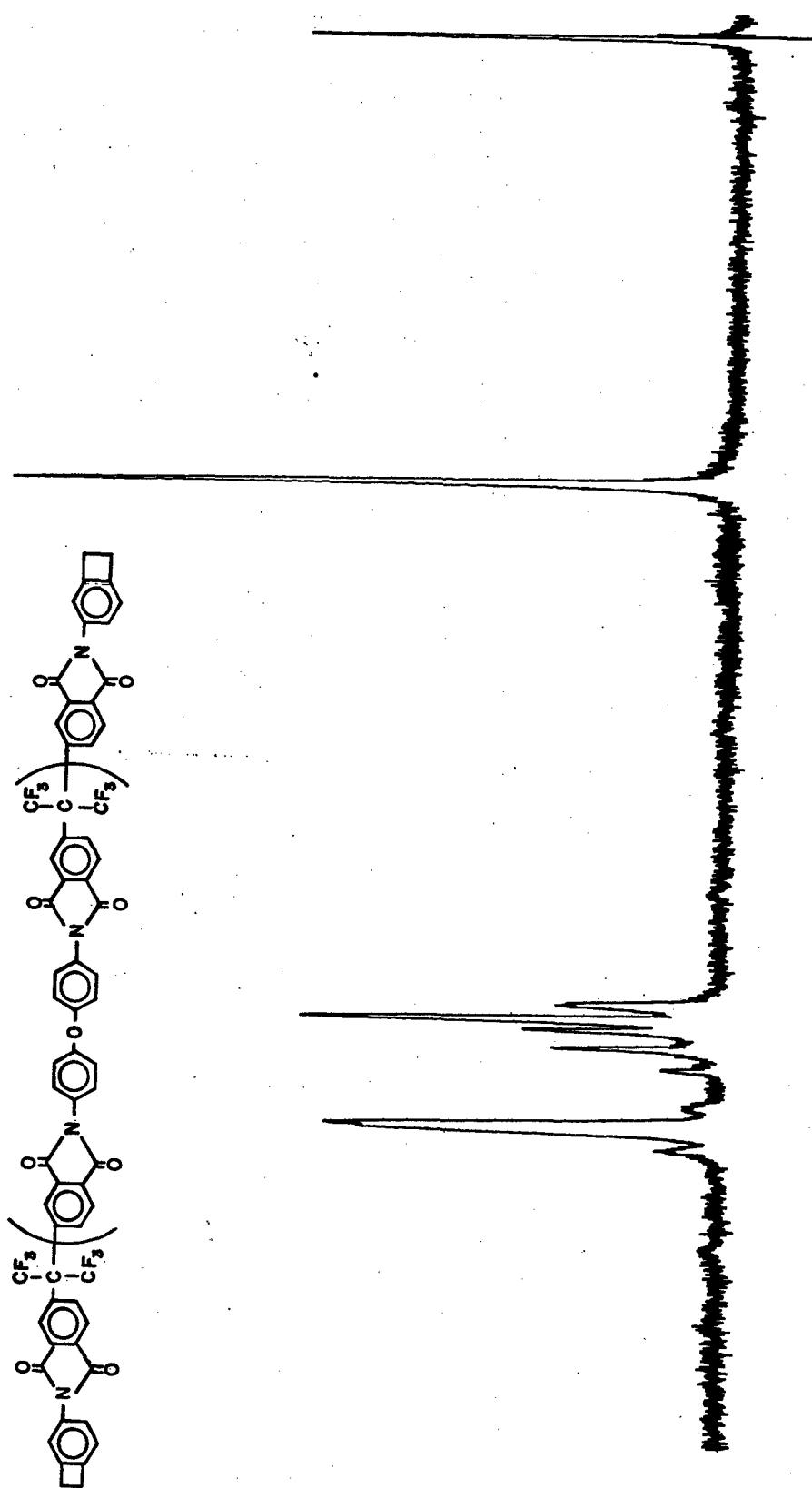


Figure 14.  $^1\text{H}$  NMR spectrum of oligomer (10c)

**BECKMAN**

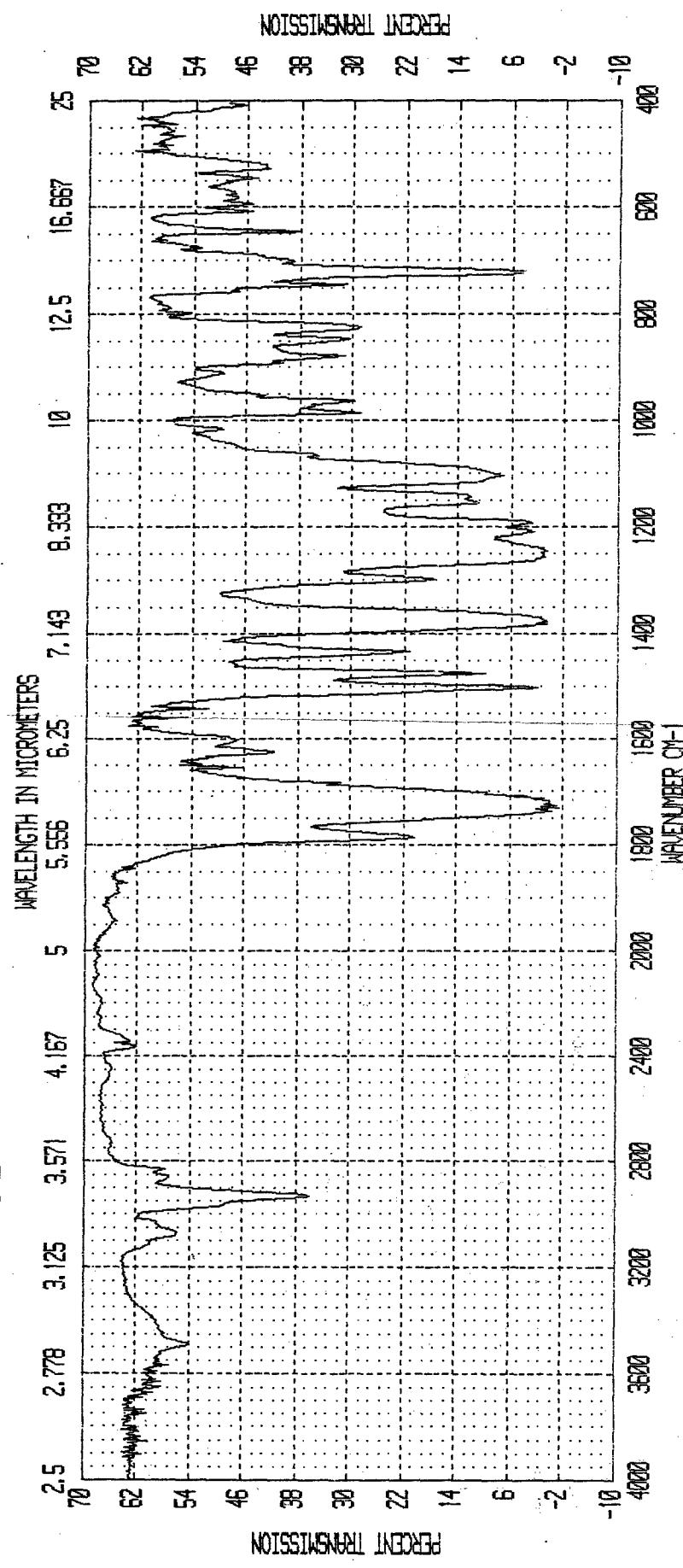


Figure 15. Infrared spectrum of oligomer (10c)

Preparation of oligomeric mixture 10d

4.08 g (9.18 mmol) of bis-2,2-(4-phthalic anhydrido) hexafluoropropane suspended under N<sub>2</sub> in acetic acid (100 ml)/toluene (80 ml) was heated to about 65°C, at which temperature all the dianhydride dissolved. 2,2'-bis(3-aminophenyl) hexafluoropropane (1.50 g, 4.49 mmol) was subsequently added neat in small portions over a period of 20 minutes, during which the temperature of the reaction mixture was maintained at 70-80°C. The resultant yellow homogenous reaction mixture was then heated to reflux and the water of the condensation was collected azeotropically. After an overnight reflux, the yellow reaction was allowed to cool to about 40°C and freshly prepared 4-aminobenzocyclobutene (2.80 g, 23.5 mmol) in about 10 ml of toluene was added. Reflux of the reaction mixture was resumed and continued for another 30 hours under N<sub>2</sub>. The dark reaction mixture was allowed to cool to room temperature and poured into 600 ml of distilled water. Extraction was performed using ethyl acetate as the extracting solvent (100 ml, then 3 x 50 ml). The organic extract was then washed with 10-percent aqueous sodium bicarbonate (500 ml) and then distilled water (2 x 500 ml). After having dried over magnesium sulfate, the organic extract was subjected to rotary evaporation to remove all the solvent. The fluffy gray crude product was then dissolved in methylene chloride and the resultant solution was filtered through a bed of silica gel (40 g), washing with methylene chloride until the filtrate was almost colorless. The yellow filtrate was rota-evaporated to remove about half the volume of the solvent. Hexane was added to gradually precipitate out light tan microcrystalline solid. The solvents were further removed and the product was finally collected, washed with hexane, and dried in vacuo at -60°C for two days. Yield: 7.60 g. Another batch of the oligomer was prepared similarly except

the purification step. Thus, 5.75 g (12.94 mmol) of bis-2,2-(4-phthalic anhydrido) hexafluoropropane, 2.06 g (6.16 mmol) of 2,2-bis(3-aminophenyl) hexafluoropropane and 3.84 g (32.23 mmol) of 4-aminobenzocyclobutene were reacted in 150-ml acetic acid/200-ml toluene mixture. After the usual work-up as described above, the crude product was dissolved in minimal amount of methylene chloride and the resultant solution was passed through a small column containing about 20 g of silica gel. The column was then eluted with methylene chloride until all fluorescent material was collected. Removal of the fractions collected led to the isolation of 8.04 g of yellow microcrystalline solid as the pure product. Analysis of HPLC indicated the following oligomeric composition:  $n = 0$ , 34.8 percent;  $n = 1$ , 28.9 percent;  $n = 2$ , 15.2 percent;  $n = 3$ , 7.2 percent,  $n = 4$ , 4.7 percent.  $^1\text{H}$  NMR (Figure 16), IR(KBr) (Figure 17).

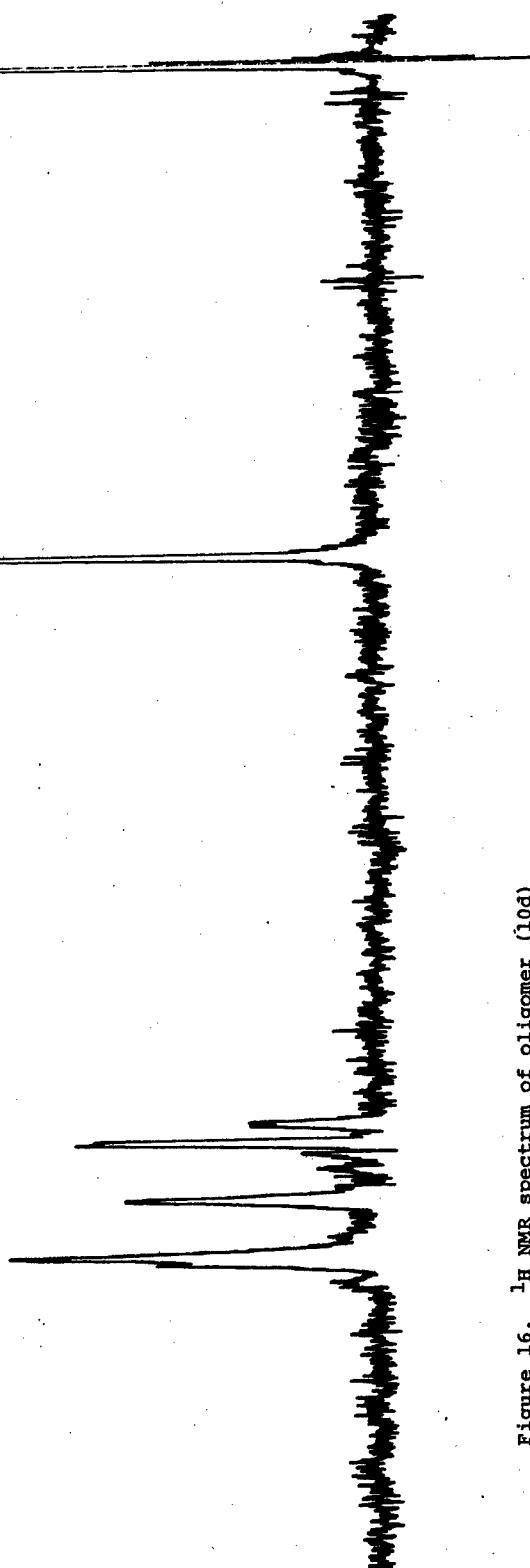
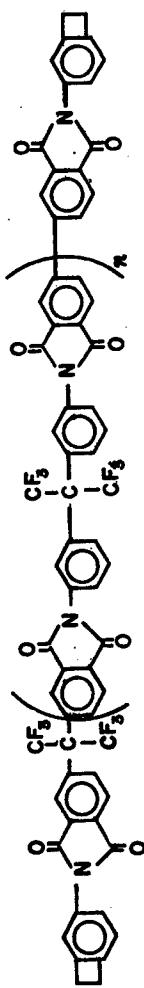


Figure 16.  $^1\text{H}$  NMR spectrum of oligomer (10d)

**BECKMAN**

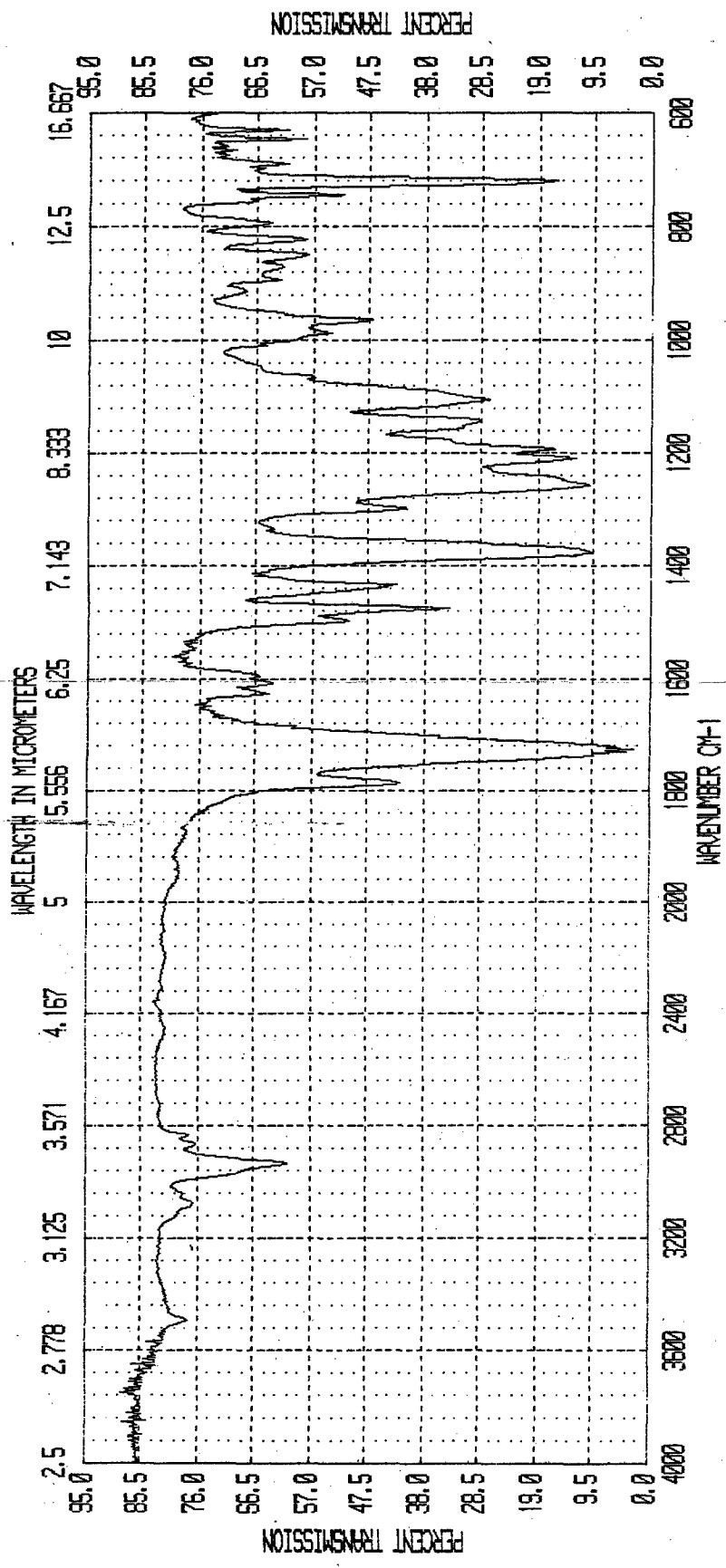


Figure 17. Infrared spectrum of oligomer (10d)

#### REFERENCES

1. R. J. Swedo and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed. 17, 2815 (1979).
2. J. K. Stille, Pure Appl. Chem. 50, 273 (1978), (b) W. Vancraeynest and J. K. Stille, Macromolecules 13, 1367 (1980).
3. F. W. Harris, K. Sridhar, and S. Das, Polym. Preprint 25 (1), 110 (1984).
4. The correct name recommended by IUPAC is 1,2-dihydrobenzocyclobutene.
5. W. Oppolzer, Synthesis 793 (1978).
6. M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, 1967, Chap. 6, pp 180-218.
7. I. Klundt, Chem Rev. 70, 471 (1970).
8. V. Boekelheide, Accounts Chem. Res. 13, 65 (1980).
9. R. P. Thummel, ibid, 13, 70 (1980).
10. T. Kametami and H. Nemoto, Tetrahedron, 37, 3 (1981).
11. Some of our results have been presented to the Polymer Chemistry Division, Am. Chem. Soc., see L. S. Tan and F. E. Arnold, Polymer Preprint 26(2), 176 (1985).
12. M. P. Cava and D. R. Napier, J. Am. Chem. Soc. 78 500 (1956).
13. A. Sanders and W. D. Giering, J. Org. Chem. 38, 3055 (1973).
14. J. B. F. Lloyd and P. A. Ongley, Tetrahedron, 20 2185 (1964).
15. L. Horner, H-G Schmelzer and B. Thompson, Chem. Ber. 93, 1774 (1960).
16. F. R. Jensen, W. E. Coleman and A. J. Berlin, Tet. Lett 15 (1962).
17. L. A. Errede, J. Am. Chem. Soc., 83, 949 (1961).
18. R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, 1971, Boekelheide had also suggested the initial formation of 11, followed by its isomerization of 15 at higher

- temperature. However, the mechanism for such isomerization was not elaborated. See V. Boekelheide, Acct. Chem. Res., 13, 65 (1980).
19. Note: Both "Cycloaddition" and "linear addition" terms are used to describe the structural uniqueness of each polymeric representation and do not implicate the mechanisms from which they arise.
20. H. H. Gibbs, Proceedings, Soc. Adv. Materials and Processing Engineering, 20, 212 (1975).
21. R. J. Jones and M. K. O'Rell, U.S. Pat. 4, 196, 277 (to TRW, Inc.).
22. H. R. Lubowitz, U.S. Pat. 3, 812, 159 (to TRW, Inc.).
23. While this paper was in preparation, similar work involving bis-benzocyclobutene had appeared in patent literature, see R. A. Kirchhoff, U.S. Pat. 4, 540, 763 (to Dow Chemical Co.).